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EXTRACTION AND CHARACTERIZATION OF CRUDE OILS FROM PRIMARY AND ENHANCED RECOVERY

Final Report

by

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EXECUTIVE SUMMARY

Produced oil samples from an in situ oxygen combustion process at Wolf Lake, Alberta were physically and chemically characterized in detail. The properties of these samples were compared to those of a core sample from the same field prior to initiation of the fire flood. The objective of this work was to assess the effects of this in situ recovery process on the quality of the produced oil, with particular emphasis on the subsequent upgrading process.

A number of analytical techniques were applied to the whole oil samples and their distillation cuts and chromatographic fractions. The gas chromatography - mass spectrometry (GC-MS) technique was a major analytical tool in this study.

Relative to the core sample, the whole oils produced during the in situ combustion process exhibited a decrease in density and viscosity, the onset of which occurred early in the production cycle. These decreases correlated with increases in the naphtha and middle distillate cuts from the distillation.

The increased naphtha content of the produced oil samples relative to the core sample suggests that the former are diluted with lighter

material formed near the fire front by thermal cracking. The total ion chromatograms of the naphtha distillation cuts reveal an increase in low boiling material in the oil produced during the fire flood process, consistent with the previous argument. The reconstructed ion chromatograms for open chain paraffins show the appearance of C_6 to C_{11} n-alkanes in the produced oil samples, again in accord with dilution by volatile, thermally cracked compounds. A GC-MS compound type analysis also indicates an increase in lighter molecules in the production samples relative to the core material.

The middle distillate cut increased from 18% of the whole oil in the core sample to as much as 30% in the produced oil samples. The physical properties of the oil are likely most affected by the large increase in this cut, as evidenced by the decrease in density and viscosity of the produced oil relative to the core sample. Chromatographic fractions 2, 3, and 4 exhibit a shift towards lower molecular weight compounds within a number of different compound classes which indicates a general "lightening" or "upgrading" of the middle distillate cut.

Both the wt% of the gas oil distillation cut and the wt% of the constituent chromatographic fractions underwent some modest changes over the time period of the study. However, there do not appear to be any consistent trends in this data and no obvious correlation to the

physical properties of the whole oil samples or the naphtha and middle distillate cuts. These changes in the gas oil cut likely reflect the complexity of the mechanisms of oil movement in the formation.

The amount of distillation residue is reduced in all of the production samples relative to the core sample in proportion to the increased naphtha and middle distillate content. The asphaltene content of the residue cuts shows only a small increase, which indicates that any asphaltenes produced by low temperature oxidation are not appearing in the produced oil.

It is concluded that the oil produced from this field pilot is upgraded based on the reduction in density and viscosity of the whole oil and the marked increase in the material boiling in the naphtha and middle distillate ranges. Evidence for this upgrading was observed in all four distillation cuts. The quality of the oil produced during the period of the in situ combustion process under consideration would not be expected to introduce any major problems in the subsequent upgrading process.

RESUME

Des échantillons de pétrole, produits par une méthode de combustion d'oxigène in situ en opération à Wolf Lake en Alberta, furent caractérisés en détail sur le plan physique et chimique. Les propriétés de ces échantillons furent comparées à celles d'un échantillon de carottage (échantillon témoin) provenant du même gisement, prélevé avant le début de l'onde de feu (fire flood). L'objectif de ce travail consistait à évaluer les effets de cette méthode d'extraction in situ sur la qualité du pétrole produit; une attention particulière fut portée à l'étape d'enrichissement à venir.

Plusieurs techniques analytiques furent appliquées aux échantillons de pétrole bruts ainsi qu'aux fractions de distillation et de chromatographie. La technique de chromatographie en phase gazeuse et spectrométrie de masse (GC - MS) fut un outil de première importance dans cette étude.

Les pétroles bruts produits au cours de la méthode de combustion in situ ont présenté une diminution de densité et de viscosité, par rapport à l'échantillon témoin. Cette diminution est apparue tôt dans le cycle de production. Ces diminutions ont pu être corrélées aux augmentations de naphte et de distillat intermédiaire observées lors de la distillation.

L'augmentation du contenu en naphte des échantillons-tests de pétrole par rapport à l'échantillon témoin suggère que ces premiers sont dilués par des matériaux plus légers formés par craquage thermique près de la ligne de feu. Les chromatogrammes d'ions totaux des fractions de naphte révèlent une augmentation du matériel à faible point d'ébullition dans le pétrole produit au cours de la méthode par combustion, ce qui est consistant avec l'argument précédent. Les chromatogrammes d'ions reconstruits des paraffines à chaîne ouverte montrent l'apparition de n-alcanes de C_8 à C_{11} dans les échantillons de pétrole; ceci est en accord avec la dilution par des composés volatiles craqués thermiquement. Une analyse typique d'un composé, par GC-MS, indique aussi une augmentation en molécules plus légères des échantillons de production par rapport à l'échantillon témoin.

La quantité de distillat intermédiaire a augmenté de 18% à 30% dans l'échantillon de production par rapport à l'échantillon témoin. Il semble que les propriétés physiques du pétrole sont les plus touchées par l'augmentation importante de cette fraction, tel que l'a démontrée la diminution de la densité et de la viscosité du pétrole produit par rapport à l'échantillon témoin. Les fractions chromatographiques 2, 3 et 4 montrent une réduction en poids moléculaire des composés qui peuvent appartenir à des classes différentes, ce qui indique un "allègement" général ou "enrichissement" du distillat intermédiaire.

Le % (en poids) de la coupe de gas oil ainsi que le % (en poids) des constituants des fractions chromatographiques ont subi des

variations mineures au cours de cette étude. Toutefois, il ne semble pas y avoir eu de tendances marquées de ces données ni de corrélation évidente avec les propriétés physiques des échantillons de pétrole brut ou des fractions de naphte et de distillat intermédiaire. Ces variations de la fraction de gas oil réflètent probablement la complexité des mécanismes de déplacement du pétrole dans le gisement.

La quantité de résidu de distillation de tous les échantillons de production par rapport à l'échantillon témoin est réduite proportionnellement à l'augmentation du contenu de naphte et de distillat intermédiaire. Le contenu en asphaltène du résidu montre seulement une petite augmentation, ce qui indique que toutes les asphaltènes produites par oxydation à basse température n'apparaissent pas dans le pétrole produit.

En conclusion, le pétrole produit à partir de ce gisement pilote a été enrichi, ceci étant démontré par la réduction de densité et de viscosité du pétrole brut et par l'augmentation marquée de matériel présent dans la zone du naphte et du distillat intermédiaire. Cet enrichissement a été mis en évidence dans les quatre coupes de distillation. On ne prévoit pas de problèmes majeurs liés à la qualité du pétrole produit par la méthode de combustion in situ considérée ici lors de l'étape d'enrichissement à venir.

INTRODUCTION

During the in situ combustion bitumen recovery operation, heat is needed to promote the movement of the oil in the reservoir. Chemical reactions and processes such as thermal cracking, low temperature oxidation, precipitation of asphaltenes, vaporization, condensation and coke formation are expected to alter both the bitumen in the region of the combustion zone and the produced bitumen. Many of these processes have been demonstrated in experiments in combustion tubes and in the laboratory and are expected to occur in thermal recovery operations (1-5). The commonly accepted model for in situ combustion is that when the oil in the reservoir is ignited the heat produced causes thermal cracking of the oil resulting in a laydown of coke on the sand. Very quickly after the start of the process the oil is pushed ahead of the fire front by the combustion gases and steam. The combustion process is sustained by burning of the coke. As the fire front proceeds, a zone of thermal cracking of the oil in place precedes the fire front itself. Many mechanisms and reactions such as low temperature oxidation and dilution by condensation and dissolution of vaporized material can be expected as the oil moves ahead of the fire front. In fact, reductions in viscosity and density are observed relatively early in the recovery process. Thermal cracking of the oil molecules is expected to cause opening of

naphthene rings, cleavage of alkyl chains and the associated rearrangement of hydrogens. These changes would be expected to produce the aromatization of certain naphthene rings as hydrogens are abstracted to form new, smaller compounds.

It is likely that these reactions can affect oil production and the quality of the oil. The results of detailed analyses of several samples produced by an in situ combustion process in a heavy oil reservoir in Saskatchewan, Canada were compared (6,7) to those of oil produced from the same field under primary conditions. Considerable upgrading of the oil was observed, as indicated by the almost tenfold increase in the naphtha boiling fraction of the oil and some increase in the middle distillate fraction. There was a marked increase in the aromaticity of these fractions and the appearance of open chain alkyl compounds. The present study is concerned with oil produced by an in situ oxygen combustion process from an oil sands reservoir at Wolf Lake, Alberta.

EXPERIMENTAL

The samples were collected from two in fill drilled wells from adjacent five spot patterns approximately two hundred meters apart. The samples of produced oil from Well 1, collected approximately one month apart over a period of three months, and of one sample from a second well (Well 2) were analyzed and compared to oil recovered from a core sample obtained from the same reservoir prior to the recovery process. Each production sample was dewatered by ultracentrifugation prior to analysis. The core sample was prepared by toluene extraction and may have lost some light ends even though care was taken to the point of leaving some toluene in the oil sample (0.5%).

Analyses were performed on the whole oil and its distillation cuts. Each sample was distilled into naphtha (<204° C), middle distillate (204°C-345°C), gas oil (345°C-442°C) and residue (>442°C) cuts prior to column chromatographic separation and subsequent analysis. These distillation temperature ranges are atmospheric pressure equivalent temperatures.

The density of the whole oil was determined at 25°C using an Anton Parr Model DMA60 density meter with a DMA601 measuring tube capable of measuring to six decimal places. The instrument was thermostated

using a recirculating water bath with a control accuracy of ±0.02°C. The temperature was monitored to the nearest 0.1°C.

The viscosity measurements were performed on a Brookfield Viscometer model RVT equipped with a cone and plate measuring head. The viscometer was maintained at the measuring temperatures of 25, 60 and 80°C using a water bath capable of controlling to ±0.2°C at the viscometer head.

The carbon, hydrogen, nitrogen, and oxygen analyses for most samples were performed on a Perkin-Elmer 240 Elemental Analyzer. Because of their low nitrogen content the middle distillate cut samples were analyzed using a Dohrman Chemiluminescence instrument. The sulfur was analyzed using the IP 242 method for the whole oil samples while the distillation cuts were analyzed using the ASTM D1552 procedure.

Distillation cuts of the oil were produced using a Nester Faust Spinning Band Distillation System. This system consists of a 480 mm x 7 mm column with a monel band spinning at approximately 29 rev/s. Each distillation was started at 5.0 mm Hg and reduced to 0.5 mm Hg when distillate collection became slow. All temperatures were converted to atmospheric equivalent temperatures (AET) using the Maxwell-Bonnell equation (8). The reflux rate for each distillation was 5:1.

Simulated distillation on the whole oil samples was carried out using the ASTM D-2 proposal P167 method run on a Hewlett Packard 5890 equipped with auto injection. The time slice data was collected on an HP3393 integrator and transferred to a VAX 11/750 computer for data processing. Simulated distillation on the middle distillate cut was done using the ASTM D2887 procedure. Cetane Index calculations were made using D87 correlations to calculate the necessary data for inclusion in the CGSB83/9/28 proposed method.

The acid numbers were determined following a method based on the IP213 and IP177 methods using a Metrohm Model 636 Automatic titrator with a glass and Ag/AgCl reference electrode pair.

The aromatics and olefin content of the naphtha cut was determined using the Fluorescence Indicator Method (FIA) ASTM D1319. The Conradson Carbon Residue was determined using a Micro Conradson Carbon Residue Analyzer according to ASTM 4530.

The chromatographic type separations (saturates, aromatics, polars, asphaltenes or SAPA) of the distillation cuts were performed by a method similar to that of Sawatzky (9,10). After removal of the asphaltenes with pentane the rest of the sample was separated on the column using the following solvent system. The saturates (fraction

1) were collected with 150 ml of pentane, followed by 200 ml of pentane with 5% toluene to collect fraction 2 (mainly mono-aromatics). Fraction 3 (mostly di- and poly-aromatics) was separated with 300 ml of 30% toluene in pentane followed by 300 ml of 70/30 (v/v) toluene/pentane for fraction 4 (polars I). The remaining fraction 5 (polars II) was eluted with 300 ml of a 50/50 (v/v) methylene chloride-methanol mixture. The fractions were evaporated to dryness by letting them stand uncovered overnight in a fume hood. The remainder of the solvent from the last three fractions was removed by placing in an oven at 100°C for 10 minutes.

The supercritical fluid chromatographic (SFC) determination of saturates and aromatics on the distillation cuts was done using a 250mm x 2.1 mm I.D. 5μ silica adsorbosphere column with supercritical CO_2 at 3600psi as the carrier (11). Response factors for saturates and aromatics were assumed to be equal for the naphtha, middle distillate, and gas oil cuts.

The proton and ^{13}C nuclear magnetic resonance (NMR) analysis was carried out using a Bruker WP80 NMR spectrometer.

Mass Spectral(MS) analyses were carried out on a Finnigan Mat 4500 Gas Chromatograph Mass Spectrometer. Methyl Silicone DB-5 or

Hewlett Packard P.N.A capillary columns were used for the gas chromatographic separations. The Methyl Silicone column was 25 meters by 0.21 mm with .33μ film thickness. The P.N.A. column was 30 meters by 0.25mm with a 0.1μ film thickness. Split injection was used for sample injection on each capillary column. The first 5 minutes of the DB-5 separation was isothermal at 65°C followed by temperature programming at 10°C per minute to 295°C. The helium carrier flow rate was 35 cm per second measured at 65°C. The separations on the P.N.A. column were performed isothermally at 35°C for the first 10 minutes followed by 3°C per minute to 150°C, then 10°C per minute to 200°C. The helium carrier flow rate on this column was 27 cm per second measured at 65°C.

The mass spectra were obtained using 70 e.v. electron impact (EI) ionization or nitrous oxide (N_2O) chemical ionization (CI) as specified. The scan rate was generally 0.95 seconds to scan from 33 to 500 A.M.U. The CI spectra were obtained using a Townsend discharge ionization source with N_2O at approximately 0.6 Torr at 120°C. The spectra were summed over the length of the chromatogram to give a picture of the types of chemical structures found in these samples. The response of the mass spectrometer for the different molecular weights was not determined due to lack of suitable standard compounds. It is recognized that the response drops off

with molecular weight and thus the data presented is not an accurate representation of the relative concentrations of compounds within a particular sample. The data does however represent the differences between samples and does give a semi-quantitative representation of the distribution of compound types within a sample.

The residue fraction samples were introduced into the mass spectrometer using the solids probe which was heated from 50°C to 300°C at 50°C per minute. The mass spectra were scanned from 150 to 650 AMU in 0.95 seconds and summed over the entire vaporization time.

RESULTS AND DISCUSSION

Whole Oil Analysis

Upgrading of the oil during the recovery process is inferred by some of the analytical data shown in Table 1. The decrease in the density and viscosity are consistent with the observed increase in the naphtha and middle distillate fractions from the distillation. The material boiling in the naphtha range from the core extracted bitumen consisted to a large degree of residual toluene left from the extraction procedure. The data for Well 2 indicates less alteration to the oil than the corresponding data from Well 1, suggesting that the production fluids may be moving through the reservoir preferentially toward Well 1. The elemental analysis of the whole oil shows a small increase in oxygen content in all the production samples, suggesting that there would be a corresponding increase in polar compounds such as carboxylic acids. The acid number, however, has dropped for all three samples from Well 1 with no change in Well 2, indicating that oxygen containing acids have not increased. Laboratory scale fire flood simulation experiments by Gray (12) on Cold Lake bitumen showed increased oxygen content in the net produced oil due to oxidation of the oil. However, a large fraction of the

oxygen was found to be in a non-polar form and not as acidic functional groups.

The September and November samples from Well 1 show increases in naphtha, middle distillate and gas oil cuts relative to the core samples while the October sample and that from Well 2 show a decrease in the gas oil cut. The oil produced during the recovery process is affected by a complex combination of mechanisms that are constantly changing and little can be said about these relative changes and the processes by simply looking at the properties of the whole oil. The two wells used for this study are in fill drilled wells in zones of the field from which little or no production was obtained during earlier production from this reservoir. This may add complexities to the interpretation of some of the changes observed if oil altered by previous contact with the fire front is mixed with virgin oil.

Naphtha

The naphtha content of all three samples from Well 1 is higher than that from Well 2 and the core sample suggesting that the produced oil is diluted by lighter materials from near the fire front. The olefins content of the naphtha distillation cuts by FIA (Table 2)

shows an increase with time and provides evidence for thermal cracking of the bitumen which likely also produces small aromatic molecules as indicated by the corresponding increase in the aromatics content in these samples. Analysis by SFC was also carried out and is consistent with the FIA data considering that olefins elute with the saturates by the SFC technique. As discussed in the experimental section, the SFC response factors for the saturates and aromatics were assumed to be equal. Analysis of the naphtha from the core sample was not performed because it consisted mainly of the residual toluene used to extract the oil from the sand. The changes between samples in the nitrogen and sulfur content of the naphtha cut are probably due to the production of smaller nitrogen and sulfur containing molecules by thermal cracking of the large compounds. Mass spectral analysis was not helpful in measuring these molecules because they could not be picked out from other ions of the same mass without further fractionation of the samples or use of a higher resolution MS. Substituted thiophenes and benzothiophenes were observed but without further separation could not be quantitated.

The total ion chromatogram of the naphtha cuts produced by GC-mass spectral analysis in Figure 1 shows an increase in low retention time peaks (low boiling compounds) for Well 1 relative to the core sample. Well 2 which has been shown from Table 1 to have a less upgraded

product gives a chromatogram similar to the core sample with some increase in certain ions. This data might suggest that the naphtha from Well 2 is composed primarily of light ends indigenous to the oil but increased in concentration due to vaporization near the fire front and diffusion to the production well. The naphtha from Well 1 is composed of smaller compounds produced by cracking near the fire front and produced with the oil near the production well.

Figure 2 shows the distribution of straight chain and branched (open chain) paraffins in the naphtha cut. The reconstructed chromatogram for ions of open chain compounds of the core sample shows no regular pattern characteristic of homologous alkanes. Because the core sample consists primarily of residual toluene it may not show the presence of these compounds even if they would be present in the virgin oil. Most of the ions present are probably due to fragmentation from other types of molecules. The Well 2 sample shows the presence of some C_9 ,C_{10} and C_{11} alkanes due to cracking, while the samples from Well 1 show smaller alkanes down to C_6.

A compilation of the compound types observed in the naphtha cuts by GC-MS is shown in Figure 3. The naphtha from the core derived bitumen (after subtracting the large peak due to residual toluene) shows primarily 1- and 2-ring saturates (naphthenes) and some alkyl

benzenes. Any olefins in the naphtha samples would be included in the naphthene compound classes. The September, October and November samples show the relative growth with time of the alkyl benzene and benzocycloparaffin molecules which are produced by thermal cracking.

There is also a small relative increase in open chain alkanes from the fire flood oils, corresponding to the observed appearance in the chromatogram of the regular pattern of the n-alkane homologs. There is also a relative decrease of the 1-ring naphthenes. These "new" compounds are likely produced by thermal cleavage from larger molecules such as asphaltenes and resins which contain a combination of aromatic and naphthenic rings joined together or substituted by alkyl chains. It should be noted that the naphtha cut represents only a small fraction of the total oil.

Middle Distillate Cut

The total middle distillate cut increased from about 18% of the oil from the core sample to 30% of the November sample (Table 1) from Well 1, which indicates the highest degree of alteration, with Well 2 showing an increase to almost 24%. The large increase in this cut is likely to most affect the physical properties of the produced oil and

corresponds well with the observed changes in the viscosity and density. The column chromatographic separation (Table 3) of the middle distillate fraction shows variations in saturates, aromatics and polars content. The October sample, however, exhibits the largest increase in the aromatics fraction of the middle distillate cut, as shown by both SFC and column chromatography, with a corresponding decrease in the saturates content. The aniline point and cetane index, used to evaluate a middle distillate as a diesel fuel, are both low for this sample and correlate with the higher aromatics content. The GC-MS analysis (Figure 4) of the saturate fraction 1 does not show any dramatic changes in the distribution of compound types. Some changes in relative peak heights within the groups of compounds is observed but these are small and may be due to the chromatographic separation procedure. The overall observed upgrading of the oil appears to be more a result of the increase in middle distillate content rather than any dramatic changes in the types of saturated compounds found in the middle distillate cut.

Chromatographic fraction 2 (Figure 5), which contains primarily the alkyl benzenes and the benzocycloparaffins, shows little difference in the distribution of compound classes between samples. The exception is the October sample which shows an increased concentration of lower carbon number alkyl benzenes and

benzocycloparaffins. The chromatographic data in Table 3 shows little variation in the wt% of fraction 2 between samples. Fraction 3 from the chromatographic separation (Table 3), which contains mainly di- and poly-aromatic compounds, shows a much larger variation in quantity from sample to sample. This fraction also shows dramatic increases in the unsubstituted naphthalene (C_{10}) and phenanthrene/anthracene (C_{14}) in the October sample (Figure 6). This is supported by the increase in proton and ^{13}C aromaticity as seen in tables 4 and 5, with the October sample showing the highest aromaticity for these samples. Unsubstituted aromatics give a higher NMR aromaticity than the corresponding alkyl substituted aromatics because of their higher percentage of aromatic ring carbons. The alkyl benzenes are less substituted in the October sample which is also consistent with the NMR data. A similar increase in phenanthrene is observed for fraction 4 (Figure 7) in the October sample. Mass spectral analysis of chromatographic fraction 4 (polars I) shows some other changes in composition among the samples. In contrast to the phenanthrene/anthracene content, this fraction contains a high proportion of dibenzothiophenes and a two ringed terpenoid sulfide series for all except the October sample from Well 1. The dibenzothiophene and the sulfur containing terpenoid were measured together because their molecular weights are the same, but both series of compounds were observed. This fraction only shows a

trace of naphthalenes which are not indicated in Figure 7. Both production wells show an increase in the phenanthrene/anthracene compound class (in particular the C_{14} and C_{15} members) over the core sample, which indicates the production of these molecules by thermal cracking of larger compounds. In general in this fraction we see a shift to lower carbon number compounds within each compound class except for the fluorenes, indicating a general "lightening" or "upgrading".

The relative increase in phenanthrenes/anthracenes in the production wells versus the core sample (fraction 4) appears to be correlated with a decrease in alkyl benzenes and benzocycloparaffins. This indicates that the phenanthrenes/anthracenes might be formed by reactions of benzenes and benzocycloparaffins via side-chain oxidation and subsequent ring closure (13). The increase in oxygen content from core sample to production wells supports this suggestion as does the increase in aromaticity indicated by the ^{1}H and ^{13}C NMR data.

Gas Oil Cut

The amount of the gas oil cut increased somewhat in the September and November samples compared to the core sample (Table 1) but decreased in relative proportion in the October sample and in Well 2. These

changes are difficult to explain without detailed information about the field operating parameters but they further indicate the complexity of the mechanisms of oil movement in the formation. From the viscosity of the whole oil and the naphtha and middle distillate data (Table 1) the October and November samples would be considered to be most "upgraded". As seen in Table 6, however, the chromatographic separation does not indicate this trend in the gas oil fraction. The saturates fraction of this cut (Figure 8) does, however, indicate that the October and November samples have a relatively higher proportion of open chain and one ring saturates relative to the ring compounds. Within these classes the carbon number distributions change very little.

The wt% of fraction 2 shows a large variation from sample to sample (Table 6) while only minor changes in compound type distribution (Figure 9) by GC-MS are observed.

The NMR aromaticity data shown in Tables 7 and 8 shows only minor changes in fraction 3 for all the samples. A more pronounced increase in aromaticity is observed for fraction 4 (polars I) of the November sample, which appeared most "upgraded".

Residue Cut

The amount of distillation residue is reduced in all the samples compared to the core sample in proportion to the increased content of naphtha and middle distillate boiling material. The residue shows some changes in elemental composition (Table 9) with decreased C/H ratio and slight decrease in sulfur and nitrogen content in going from the core to the produced oil samples. This may be due to fractionation of the oil as it moves through the reservoir. The data for the chromatographic fractions of the residue also indicates that changes in this portion of the oil are occurring. The changes are not easily explained without more detailed analysis and understanding of oil movement in the reservoir. The October sample which showed the largest increase in aromatics content in both the middle distillate and gas oil cuts also shows the largest amount of fraction 2 (mostly mono-aromatics) in this cut. Mass spectral analyses (Figures 10 and 11) of the volatile portions of the saturates (fraction 1) and mono-aromatics (fraction 2) show an increase in the open chain, 1- and 2-ring saturates and a shift to smaller aromatic molecules in some of the production samples compared to the core sample. The asphaltene content of the residue shows only a small increase suggesting that any low temperature oxidation to produce asphaltenes is not affecting the produced oil. Similarly no increase in polars is observed in the residue.

Conclusions

The oil produced from this field pilot is upgraded as seen from the reduction in density and viscosity of the whole oil and the more than threefold increase in material boiling in the naphtha range. The hydrocarbons boiling in the middle distillate range increased by almost a factor of two in the samples showing the highest degree of upgrading and are probably responsible for most of the changes observed in the physical properties of the produced oil. The distillation residue correspondingly decreased in the samples showing upgrading.

All four distillation cuts of the produced oil show an increase in aromaticity even though only the naphtha cut shows any appreciable appearance of "new" compounds. The GC-MS analyses show that some changes occur in all of the distillation cuts and increased aromaticity in a sample is reflected in all four cuts. The changes observed in the residue are most surprising especially when the observed increase in aromaticity of the October sample is reflected in all distillation cuts.

The general conclusion is that, except for the increase in the naphtha and middle distillate content and the increased aromaticity,

the overall quality of the produced oil would not be expected to introduce any major problems to the upgrading of this oil. The surprising absence of an increase in acid number and polar compounds suggests that for a certain period of production no major problems should be experienced due to the fire flood process. It must be recognized that there may be other wells where channeling may be occurring or that later in the production cycle more dramatic changes may be observed.

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Table 1

WHOLE OIL ANALYSIS

		Well 1			Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Density kg/m3 25°C	989.4	988.8	979.5	968.8	984.1
Viscosity cps					
25°C	49,400	12,700	1765	820	8540
60°C	1,300	557	148	93	470
80°C	372	175	59	39	159
Carbon	83.90	84.21	84.01	83.84	84.12
Hydrogen	10.67	10.31	10.22	10.77	10.58
Nitrogen	0.60	0.41	0.34	0.36	0.40
Oxygen	0.47	0.72	0.93	0.62	0.64
Sulfur	4.80	4.45	4.13	4.27	4.73
Acid No. Mg KOH/g	1.32	1.16	1.05	0.95	1.30
			Distillation		
Naphtha 115-204oC	0.8*	2.59	2.54	3.21	1.01
Middle distillate 204oC-345	17.7	19.56	24.33	30.27	23.64
Gas Oil 345-442oC	16.5	17.66	15.58	19.72	13.41
Residue >442oC	65.0	60.19	57.55	46.80	61.94

*contains residual toluene used in extraction of the oil from the core

Table 2

		NAPHTHA				
			Well 1			Well 1
		Core*	Sept.29	Oct. 23	Nov. 16	Oct. 27
Volume %		0.8	2.6	2.5	3.2	1.01
Nitrogen		<1.0	29	137	196	14
Sulfur		0.29	1.24	1.39	1.41	0.95
FIA (D1319)	Saturates		61.8	54.1	55.4	69.1
	Olefins		5.6	11.4	12.5	5.5
	Aromatics		32.6	34.5	32.1	25.4
SFC	Saturates	*	70.1	64.6	65.7	76.5
	Aromatics	*	29.9	35.4	34.3	23.5

Table 3

MIDDLE DISTILLATE

		Well 1		Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Viscosity cts.	3.99	3.66	3.47	3.69	3.6
Density g/ml	0.8908	0.8915	0.9090	0.9006	0.8950
Aniline Point	50.6	47.1	38.3	42.2	45.2
Cetane Index	38.5	38.1	33.8	36.2	37.4

CHROMATOGRPAHIC SEPARATION

Fraction 1 - saturates	57.5	54.8	45.9	52.1	56.2
Fraction 2 - aromatics	18.3	19.7	18.9	18.1	11.3
Fraction 3 - aromatics	19.2	13.5	30.4	21.9	21.8
Fraction 4 - polars	1.0	2.5	1.6	1.1	2.3
Fraction 5 - polars	1.5	4.2	1.4	2.5	3.4
	97.5	94.7	98.2	95.7	95.0
SFC					
Saturates	62.5	60.5	51.1	54.6	58.3
Aromatics	37.5	39.5	48.9	45.4	41.7

Table 4

MIDDLE DISTILLATE

PROTON NMR

		Well 1		Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Fraction 3					
aliphatic	80	75	70	76	77
aromatic	20	25	30	24	23
Fraction 4					
aliphatic	96	92	82	81	88
aromatic	4	8	18	19	18
Fraction 5					
aliphatic	95	96	*	92	95
aromatic	5	4	*	8	5

* insufficient sample

Table 5

MIDDLE DISTILLATE

C^{13} NMR

		Well 1		Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Fraction 3					
aliphatic	63	59	37	43	44
aromatic	37	41	63	57	56
Fraction 4					
aliphatic	78	72	43	50	45
aromatic	22	28	57	50	55
Fraction 5					
aliphatic	100**	86	*	72	66
aromatic	trace	14		28	34

* Insufficient sample
** Sample is suspect

Table 6

Gas Oil
Chromatographic Separation

		Well 1		Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Fraction 1 - saturates	36.8	31.7	33.7	35.7	37.8
Fraction 2 - aromatics	9.5	18.9	17.3	8.2	5.6
Fraction 3 - aromatics	40.9	35.4	40.4	37.7	46.4
Fraction 4 - polars	7.3	7.9	4.7	6.9	5.4
Fraction 5 - polars	4.2	7.9	3.7	9.3	3.9
Asphaltenes	<0.05	<0.05	<0.05	<0.05	<0.05
	98.7	101.8	99.6	97.8	99.1
SFC					
Saturates	91.1	88.7	43.3	47.8	44.2
Aromatics	8.9	11.3	56.7	52.2	55.8

Table 7

GAS OIL

PROTON NMR

		Well 1		Well 2
Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Fraction 3				
aliphatic	87	84	82	84	86
aromatic	13	16	18	16	14
Fraction 4				
aliphatic	92	82	73	72	78
aromatic	8	18	27	28	22
Fraction 5				
aliphatic	93	93	85	90	88
aromatic	7	7	15	10	12

Table 8

GAS OIL

C^{13} NMR

		Well 1		Well 2
	Core	Sept.29	Oct. 23	Nov. 16	Oct. 27
Fraction 3					
aliphatic	50	54	50	53	59
aromatic	50	46	50	47	41
Fraction 4					
aliphatic	50	58	46	43	50
aromatic	50	42	54	57	50
Fraction 5					
aliphatic	84	73	51	65	65
aromatic	16	27	49	35	35

Table 9

RESIDUE

	Core	Well 1 Sept.29	Well 1 Oct. 23	Well 1 Nov. 16	Well 2 Oct. 27
Carbon	84.50	84.26	84.26	83.72	83.60
Hydrogen	9.92	9.74	9.74	9.98	10.17
Nitrogen	0.58	0.57	0.57	0.37	0.34
Sulfur	5.78	5.33	5.28	5.39	5.61
Oxygen	1.01	1.03	1.00	1.39	1.29
Total	101.79	100.93	100.85	100.28	101.01

CHROMATOGRAPHIC SEPARATION

	Core	Well 1 Sept.29 -27	Well 1 Oct. 23 -28	Well 2 Nov. 16 Ex 32	Well 2 Oct. 27
Fraction 1 - saturates	11.2	12.1	8.8	11.5	10.8
Fraction 2 - aromatics	4.8	8.2	10.3	9.4	7.9
Fraction 3 - aromatics	19.2	18.7	19.7	19.4	22.7
Fraction 4 - polars	11.5	7.9	10.2	9.1	8.5
Fraction 5 - polars	30.0	23.0	25.6	25.0	24.4
Asphaltenes	23.5	28.8	24.1	25.3	24.4
	100.2	98.7	98.7	99.7	98.7

Table 10

RESIDUE

PROTON NMR

		Well 1			Well 2
	Core	Sept.29 -27	Oct. 23 -28	Nov. 16 Ex 32	Oct. 27 Ex-21
Fraction 3					
aliphatic	92	91	93	92	92
aromatic	8	9	7	8	8
Fraction 4					
aliphatic	88	88	89	89	89
aromatic	12	12	11	11	11
Fraction 5					
aliphatic	94	92	92	92	93
aromatic	6	8	8	8	7

Table 11

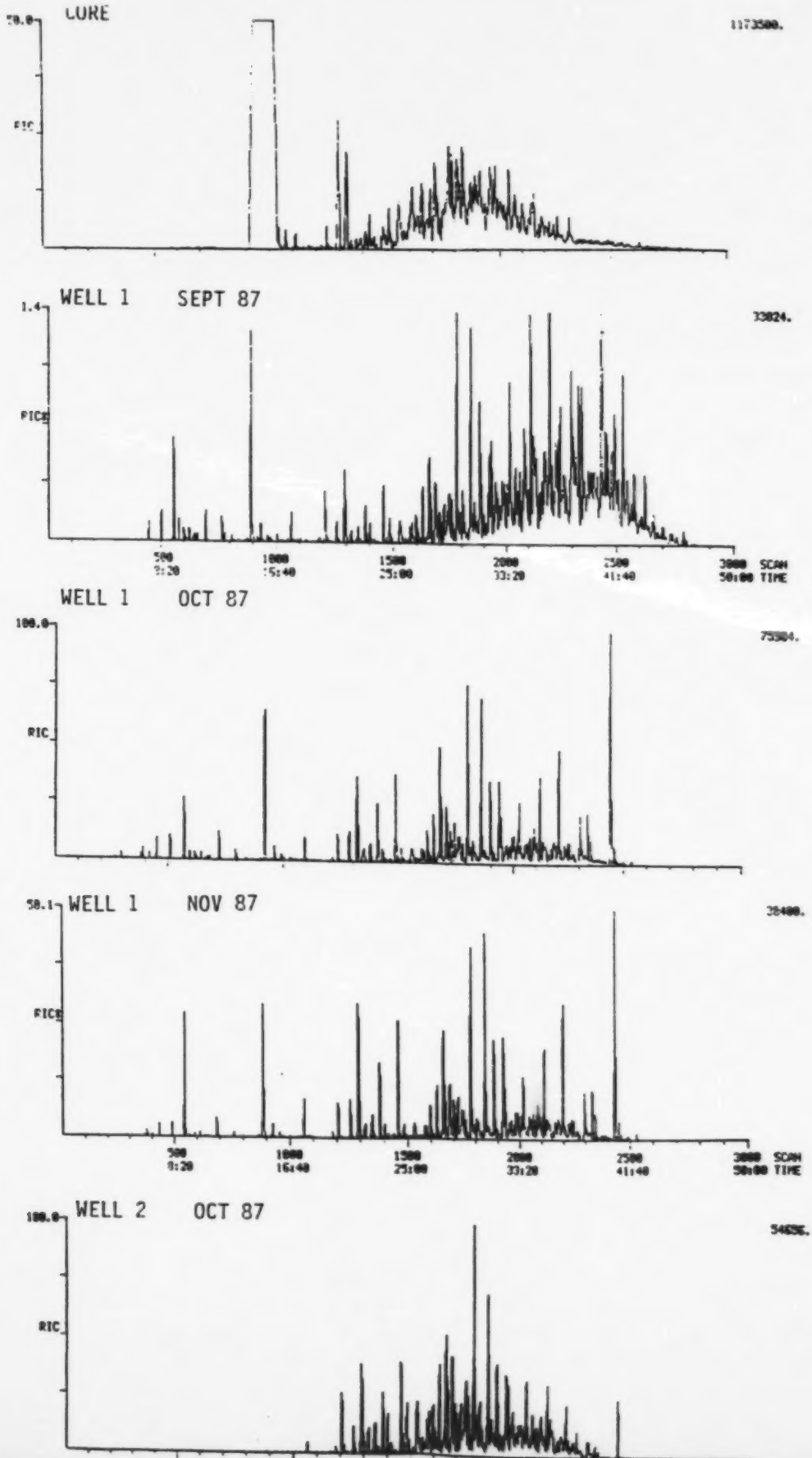
RESIDUE

C^{13} NMR

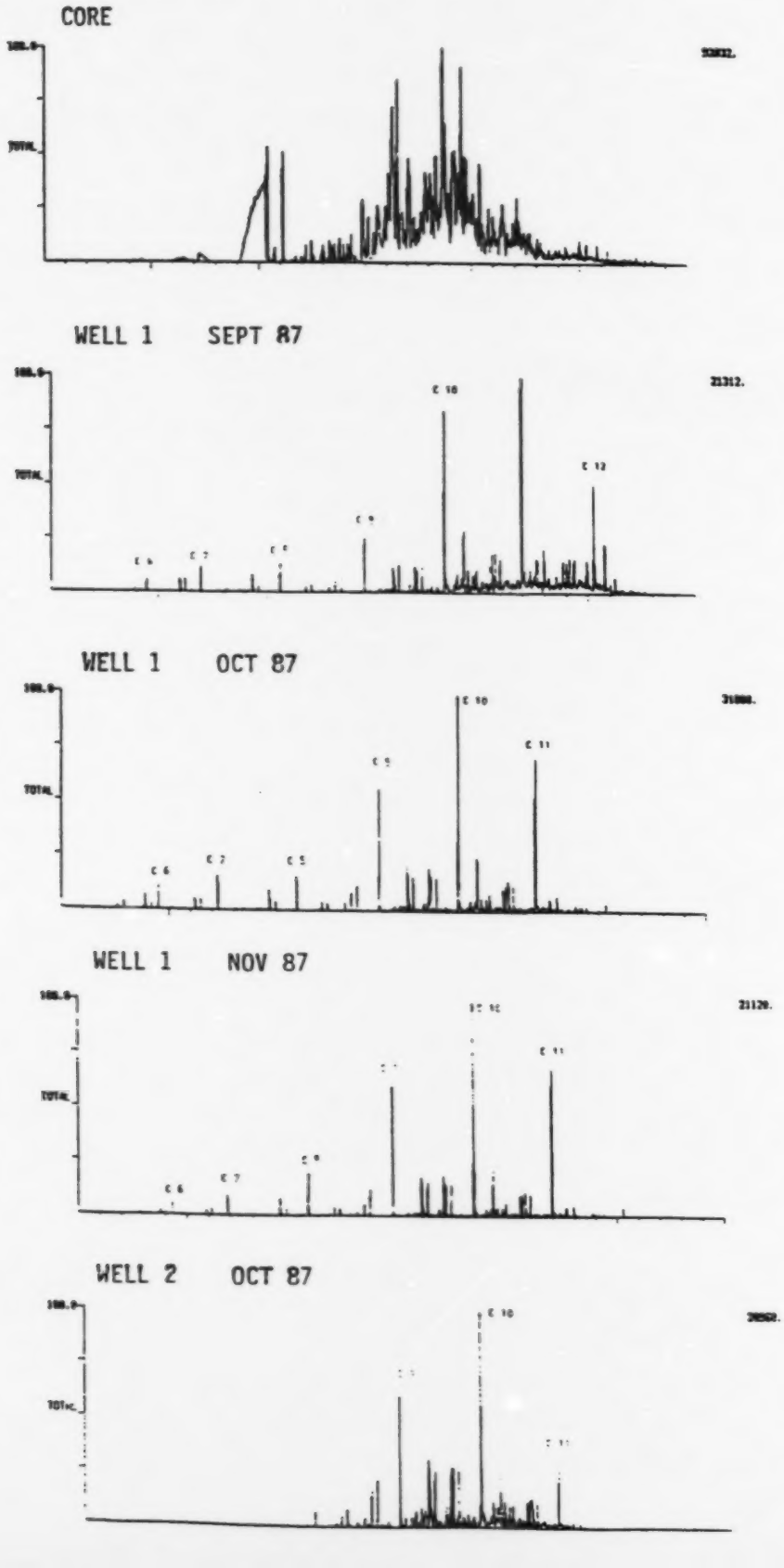
		Well 1			Well 2
	Core	Sept.29 -27	Oct. 23 -28	Nov. 16 Ex 32	Oct. 27 Ex-21
Fraction 3					
aliphatic	67	65	70	72	69
aromatic	33	35	30	28	31
Fraction 4					
aliphatic	64	57	63	58	63
aromatic	36	43	37	42	37
Fraction 5					
aliphatic	68	66	64	68	66
aromatic	32	34	36	32	34

1

The total ion chromatogram of the naphtha cut.

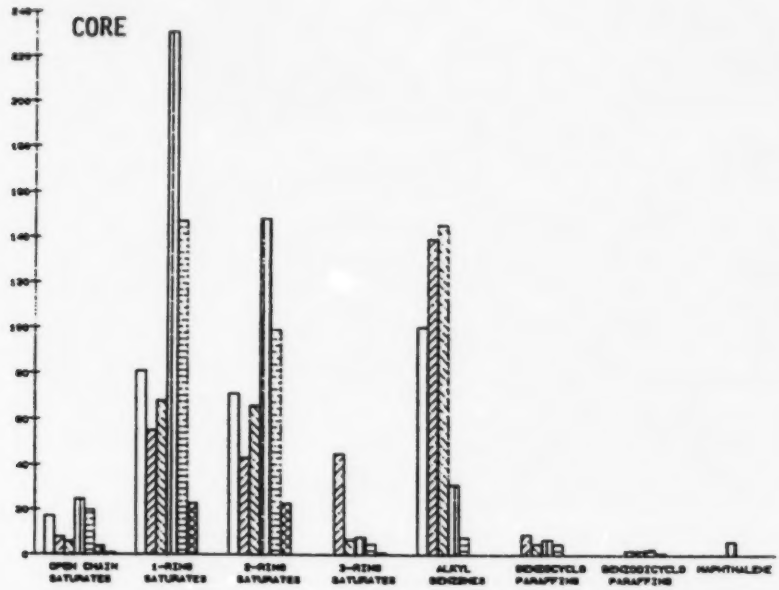


igure 2 The reconstructed ion chromatogram of the open chain saturates of the naphtha cut.



gure 3

Distribution of compound classes in the naphtha cut as determined by mass spec.



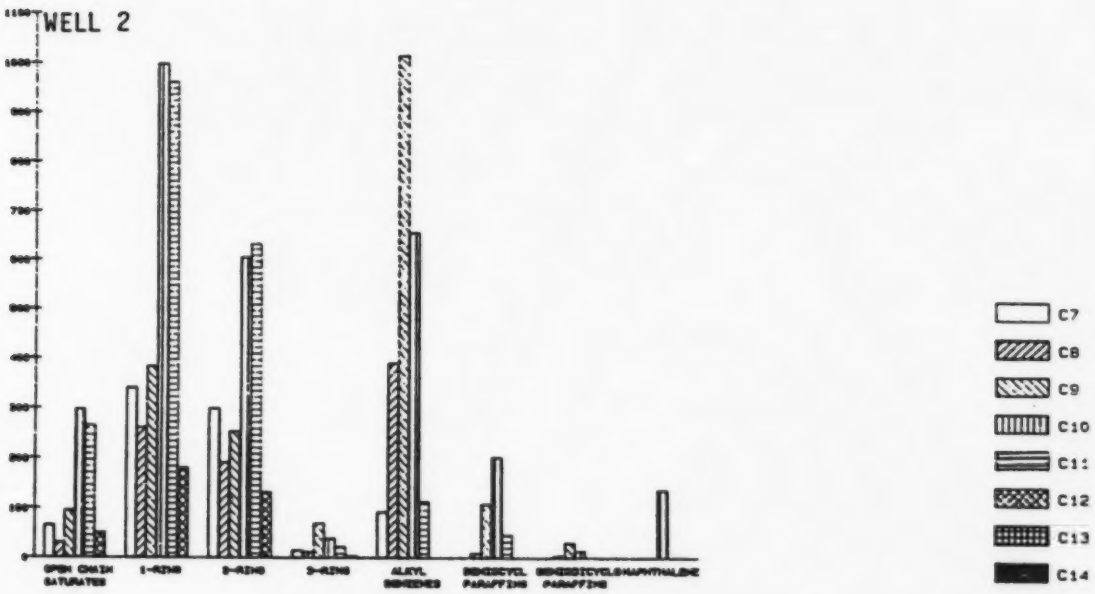
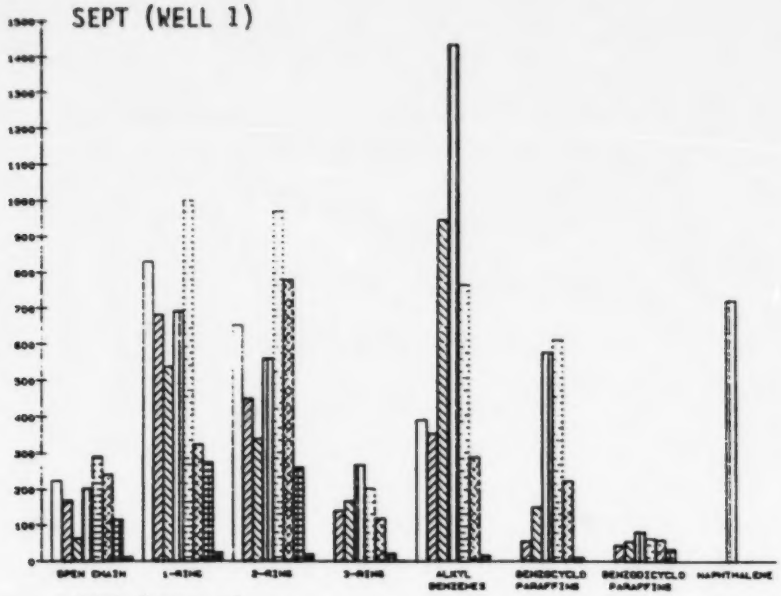
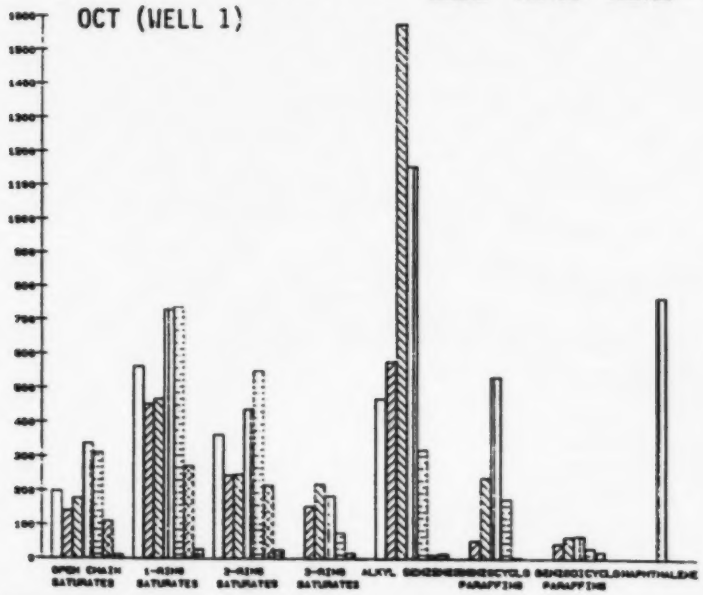
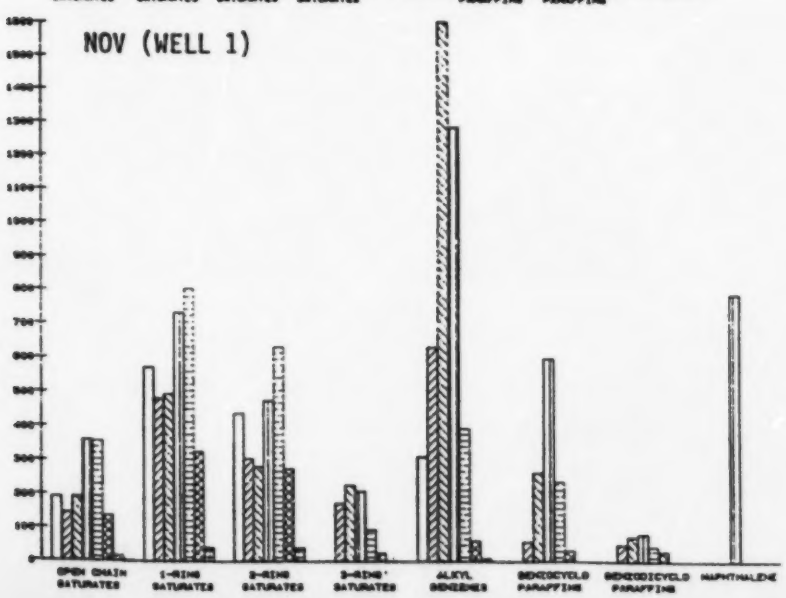


Figure 3 - con't







igure 4 Distribution of saturate compound types in the middle distillate cut.

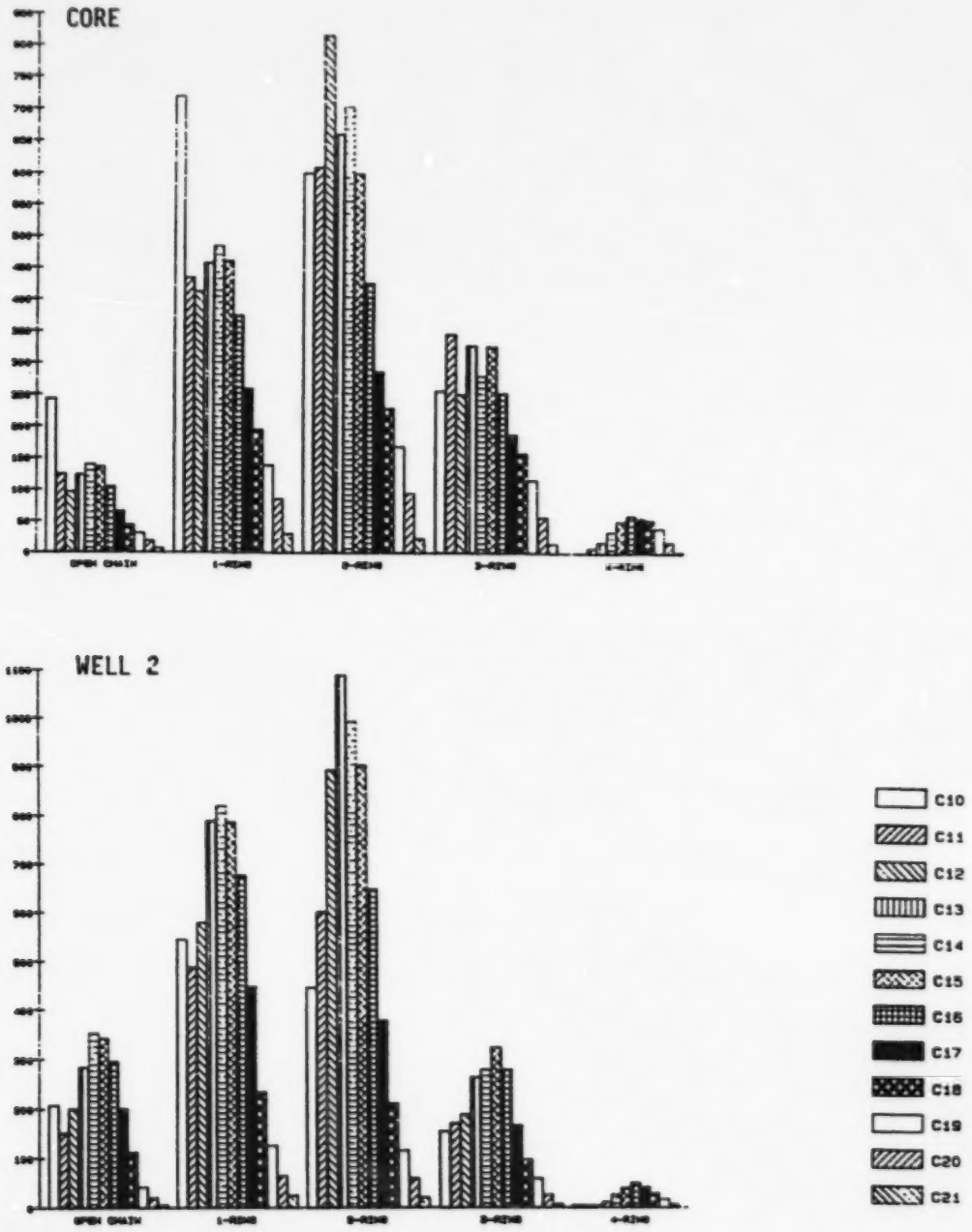
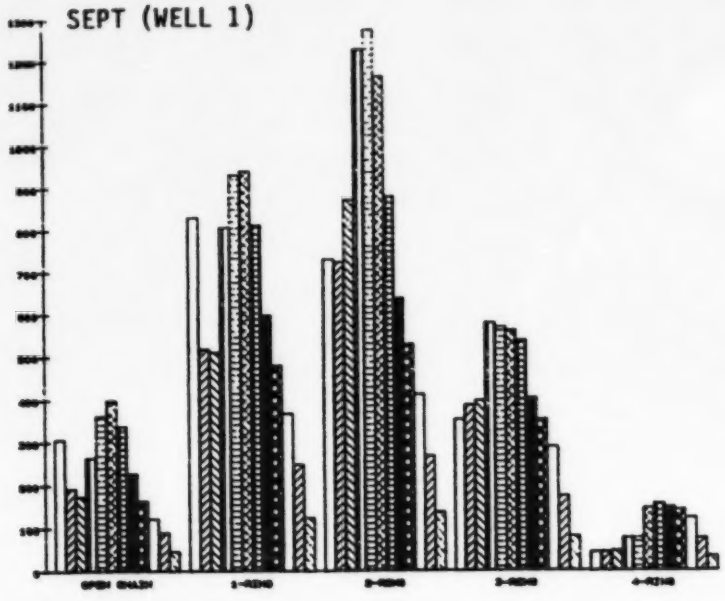
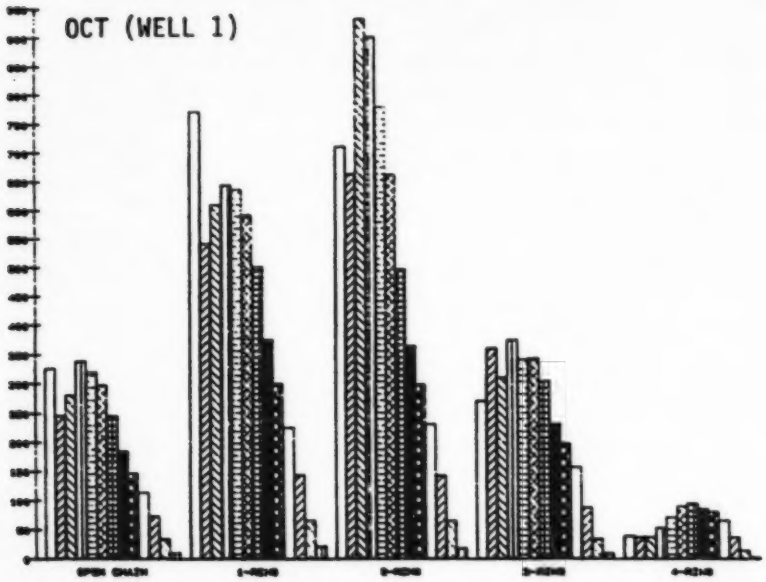


Figure 4 - con't





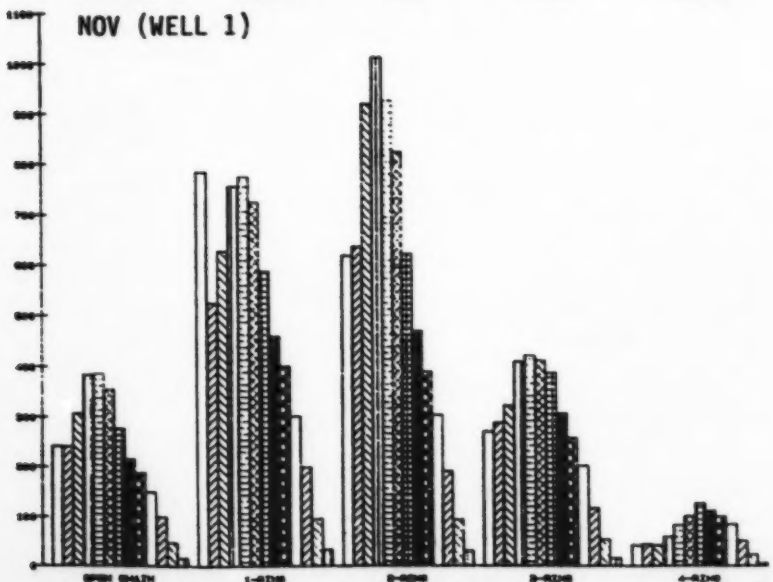


Figure 5

Distribution of compound types in the aromatics I (fraction 2) of the middle distillate cut.

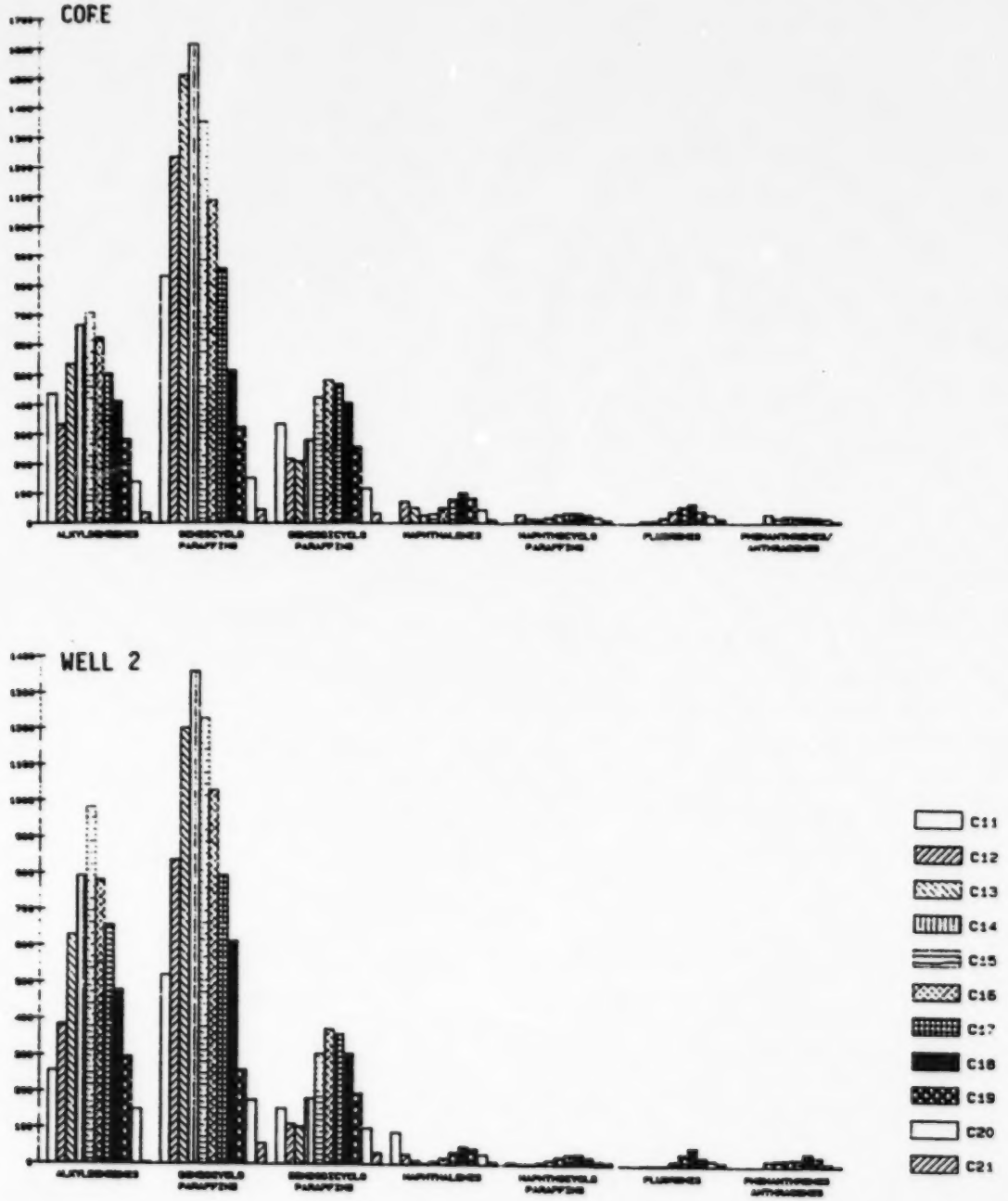
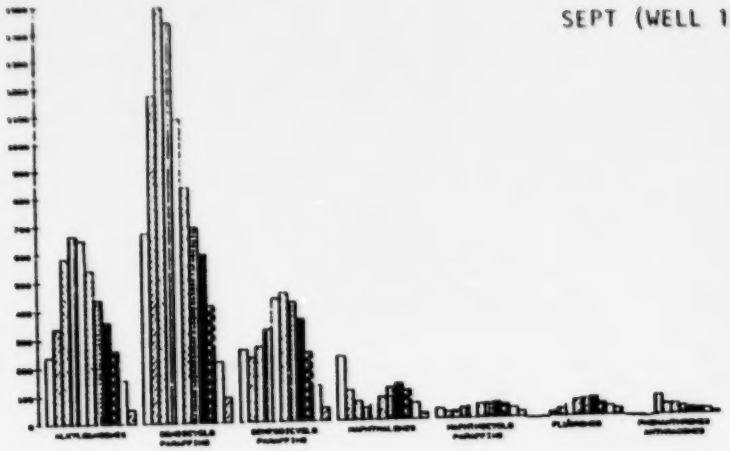
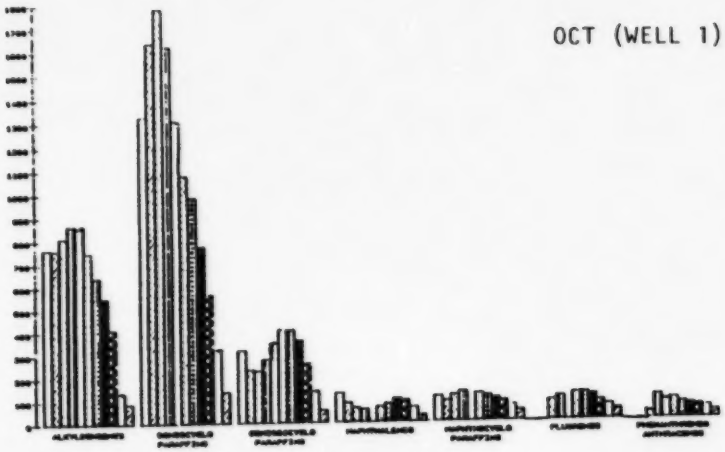


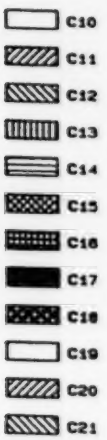
Figure 5 - con't

SEPT (WELL 1)

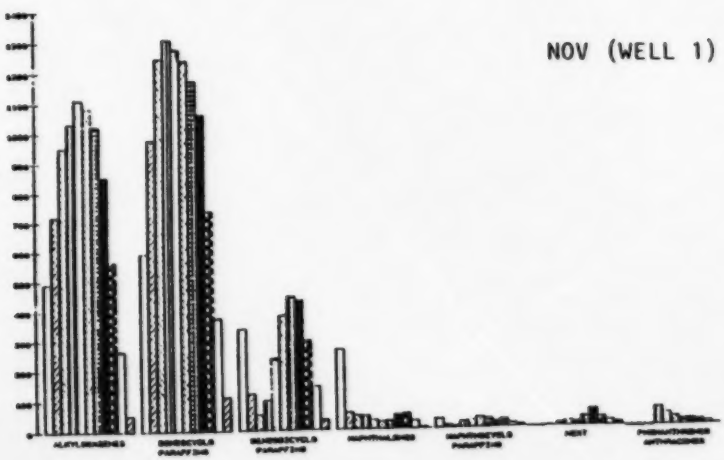


OCT (WELL 1)



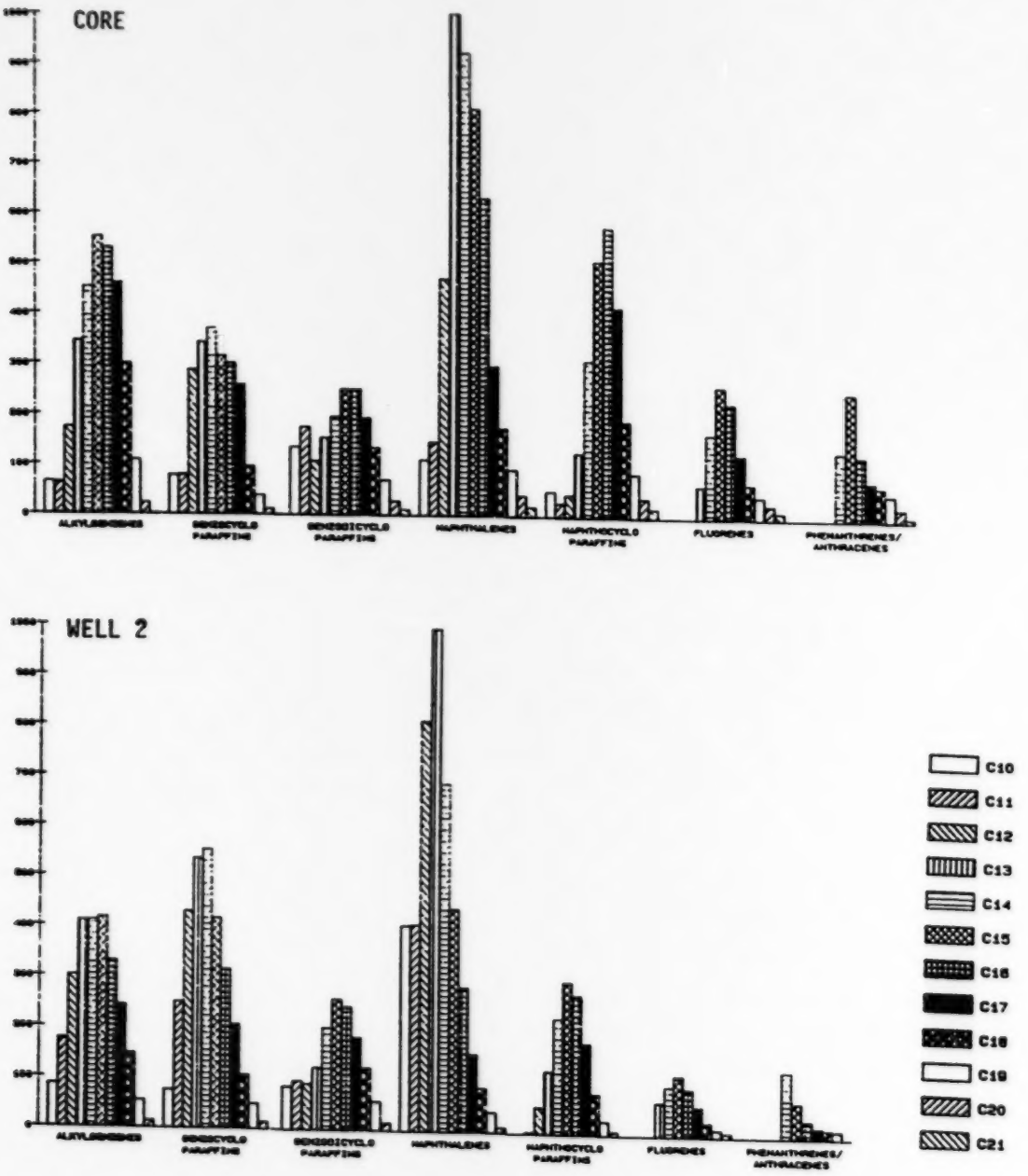


NOV (WELL 1)

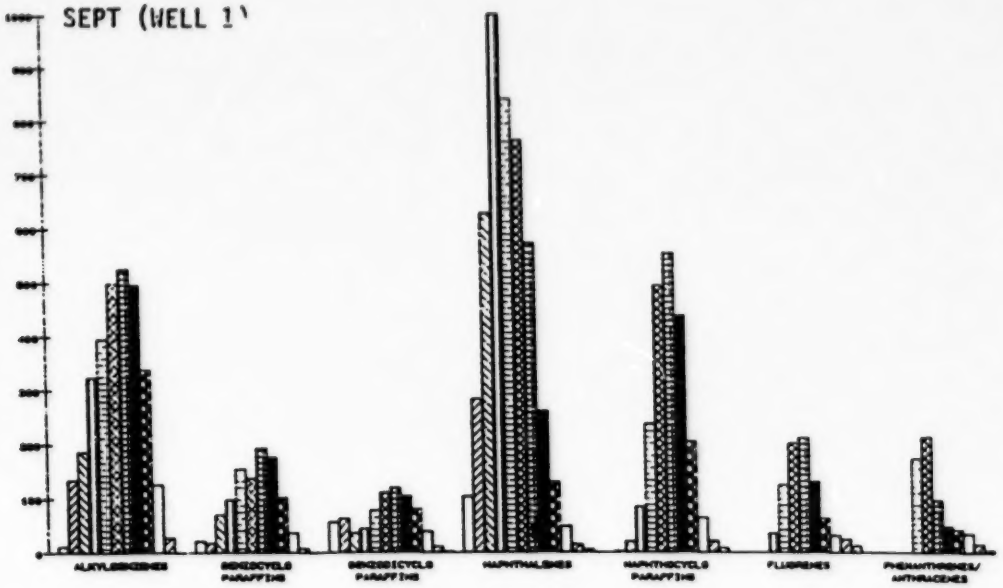


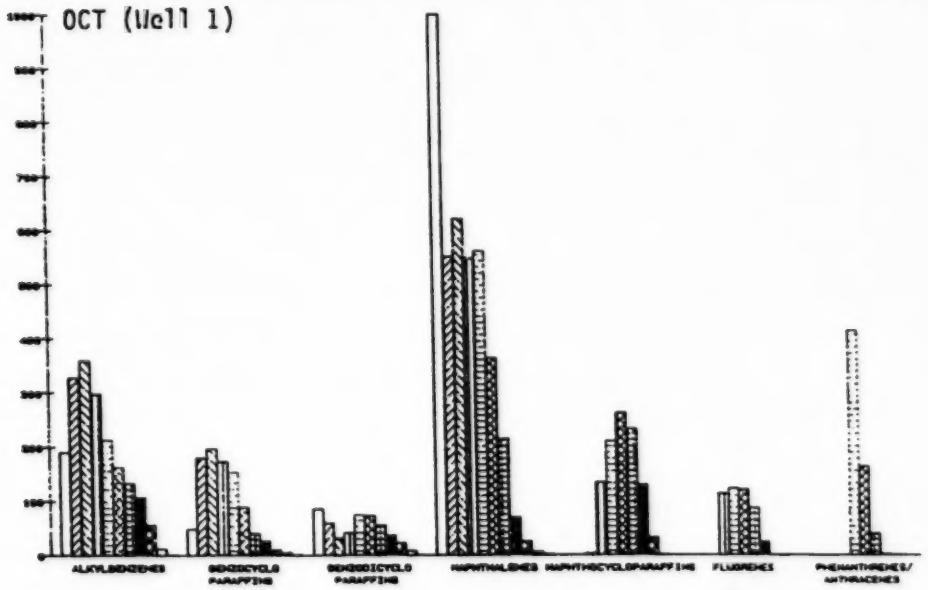
gure 6

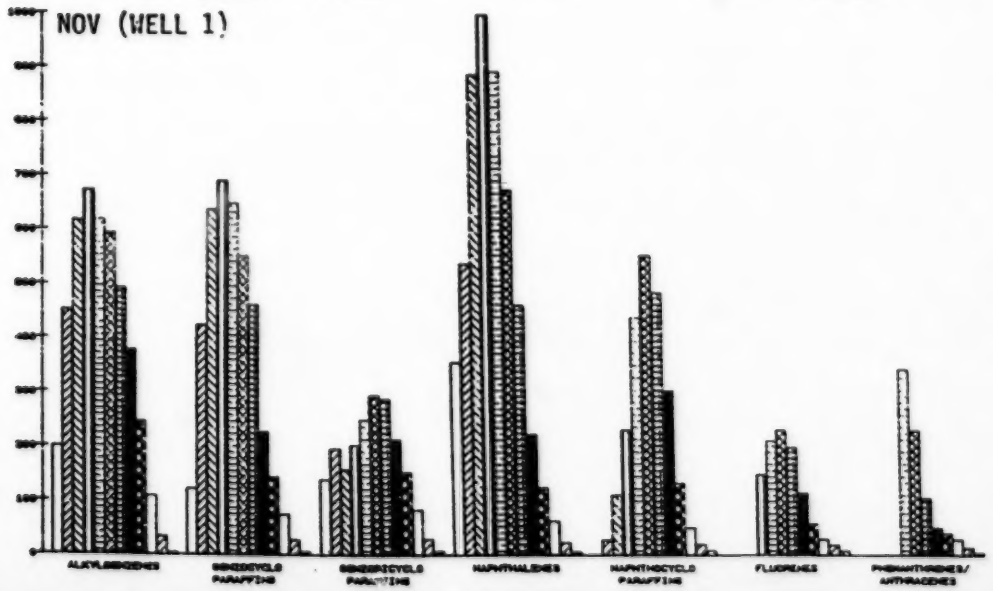
Distribution of compound types in the aromatics II (chromatographic fraction 3) of the middle distillate cut.



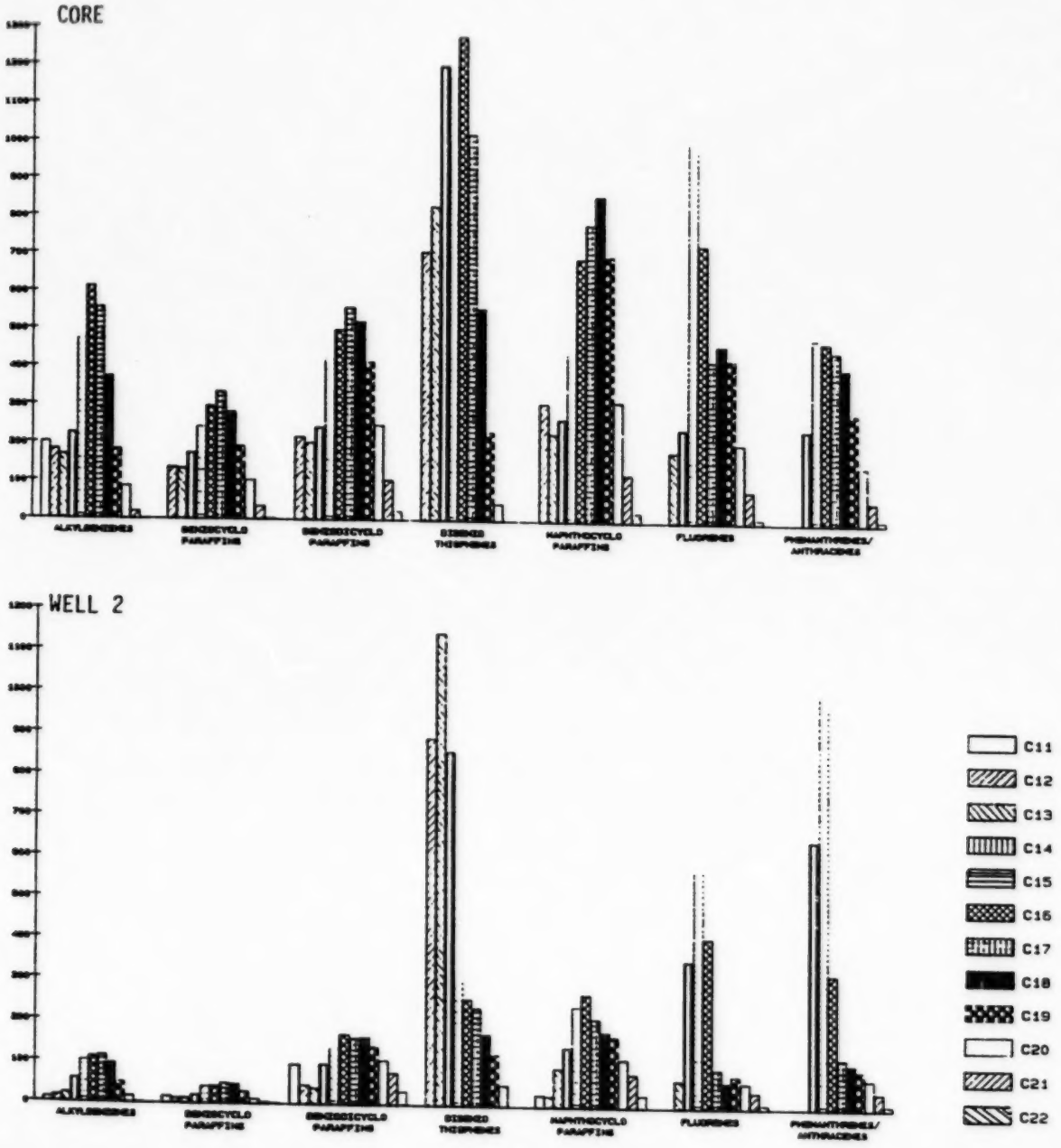
re 6 - con't



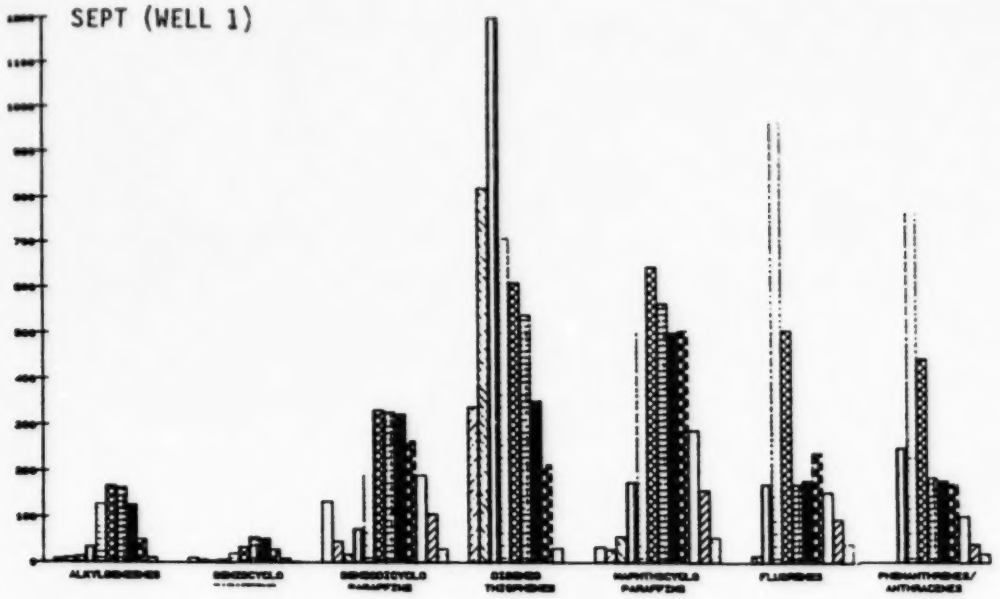


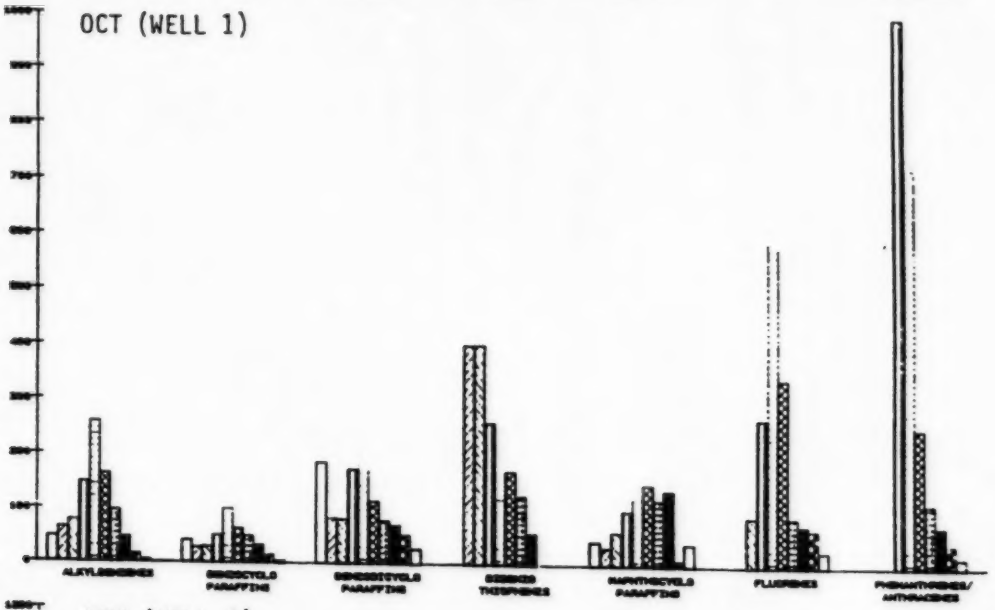


igure 7 Distribution of compound types in the chromatographic fraction 4 of the middle distillate cut.



ure 7 - con't





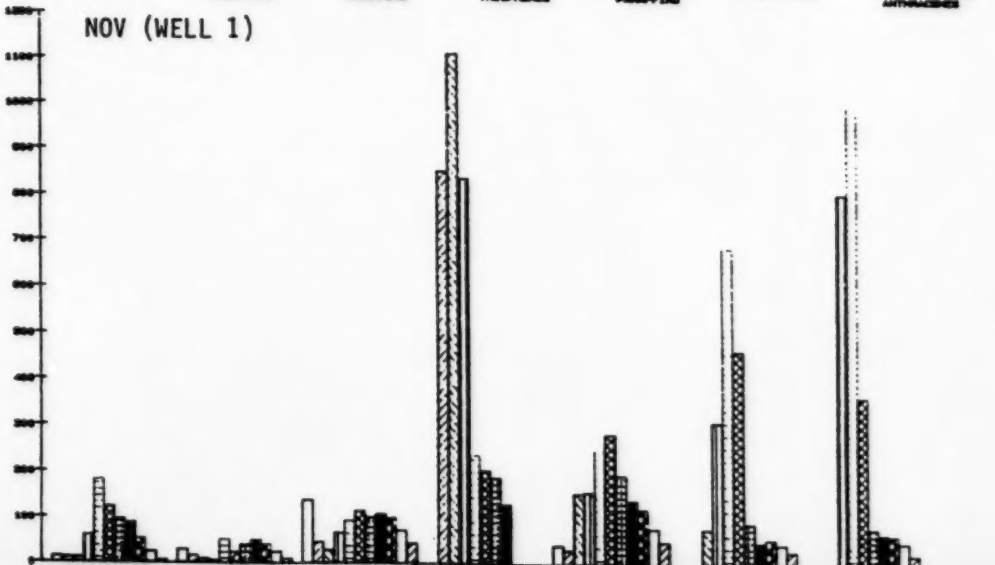


Figure 8 Distribution of compound types in the saturates fraction of the gas oil cut.

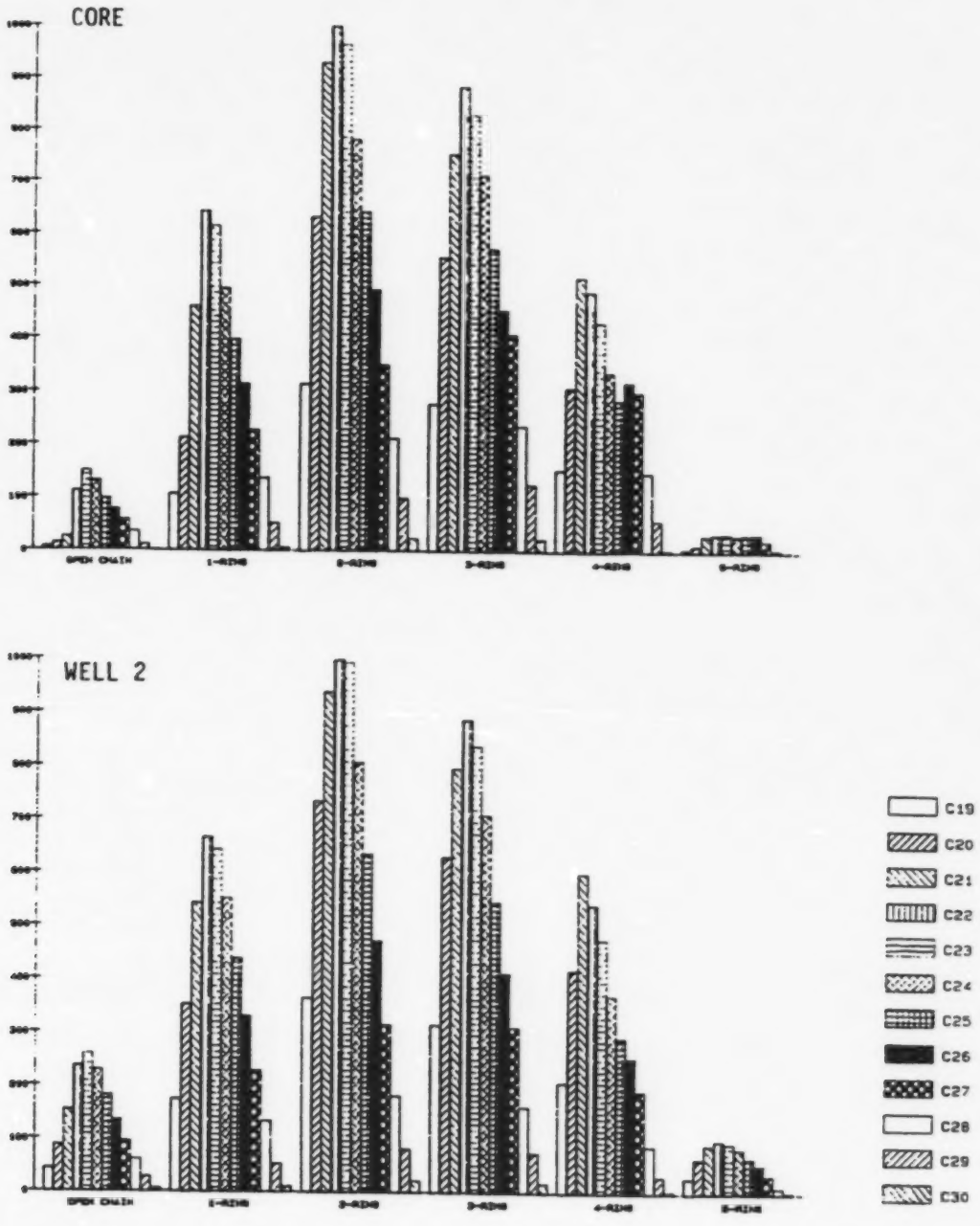
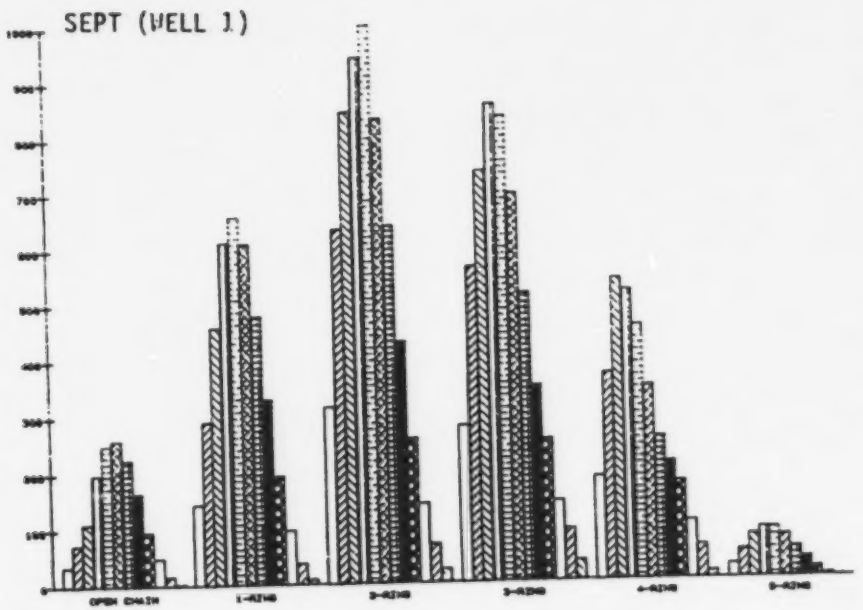
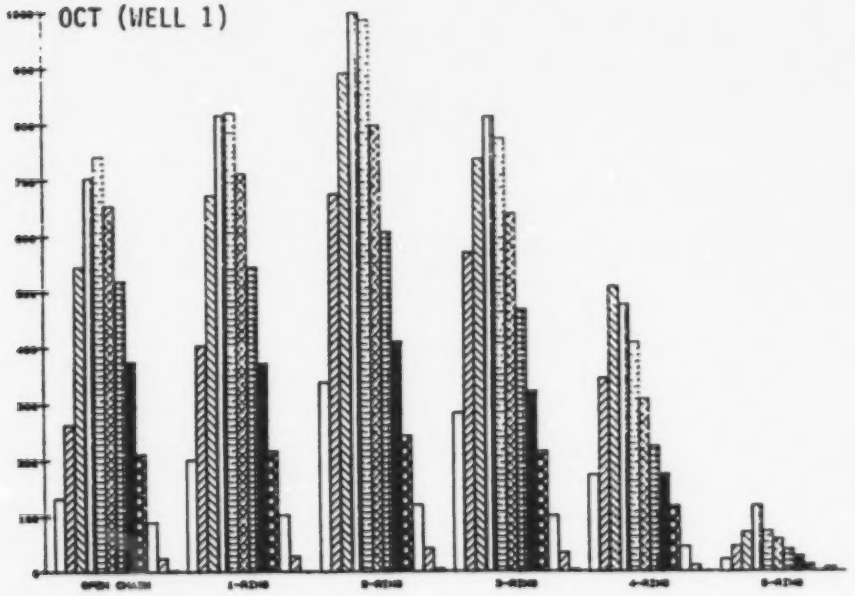


Figure 8 - con't





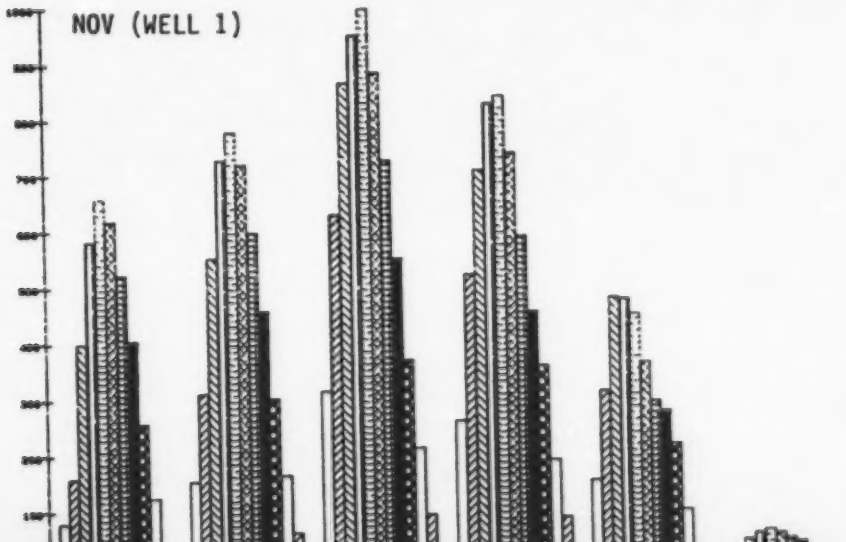
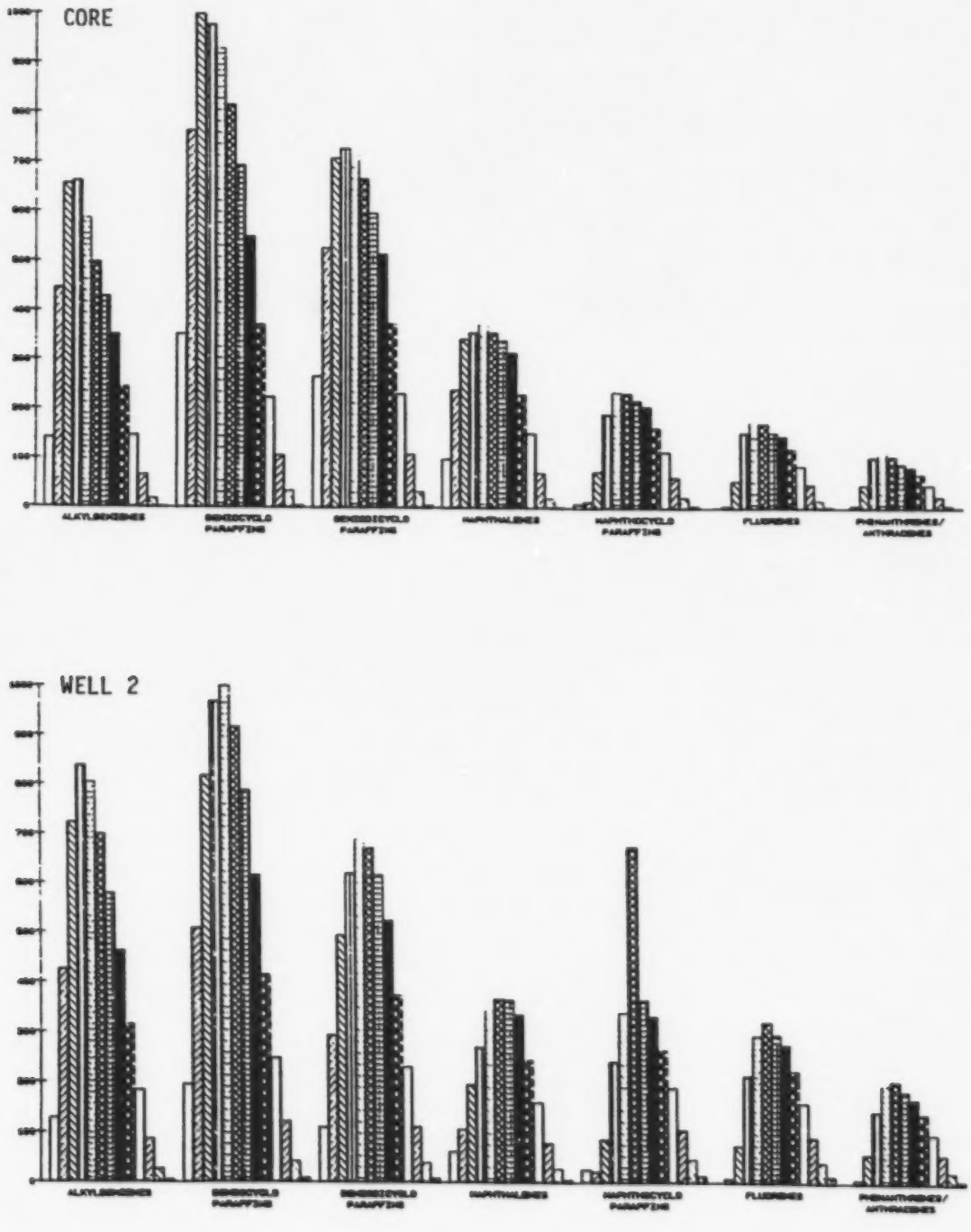
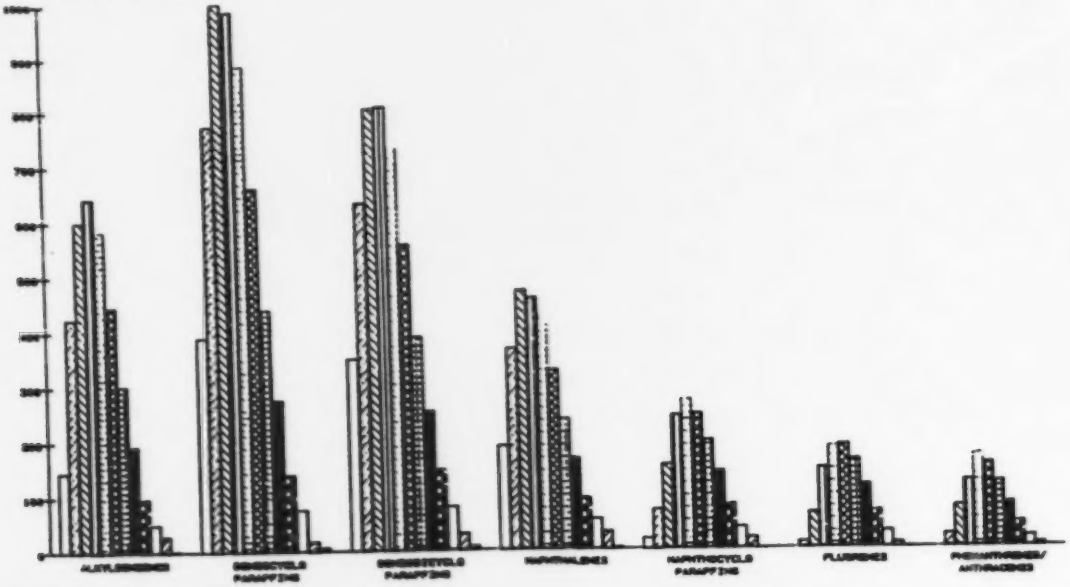


Figure 9 Distribution of compound types in the aromatics fraction (chromatographic fraction 3) of the gas oil cut.

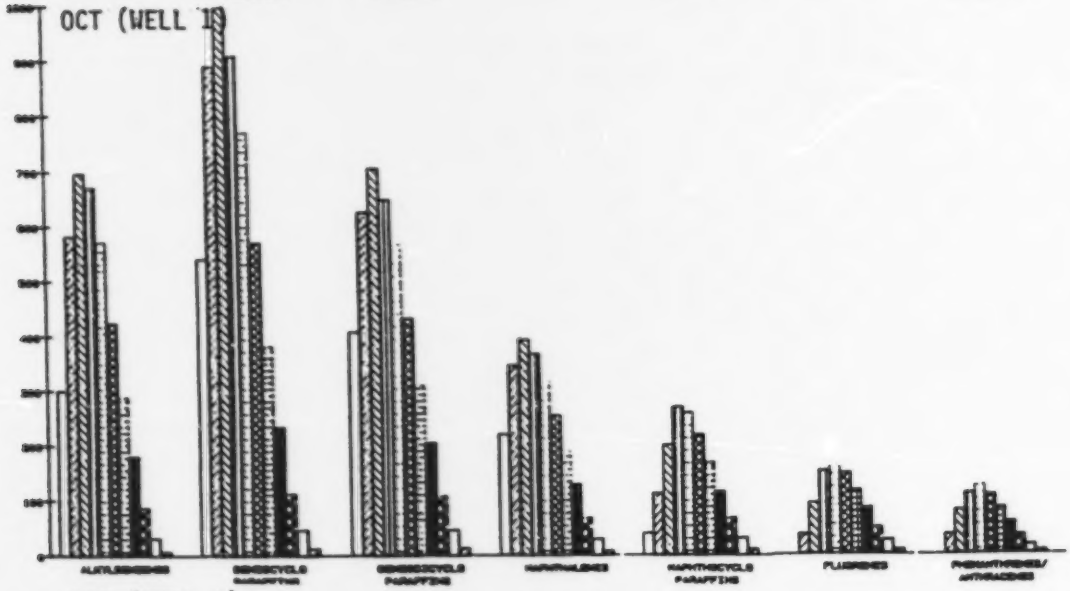


e y - con't

SEPT (WELL 1)



OCT (WELL 1)



NOV (WELL 1)

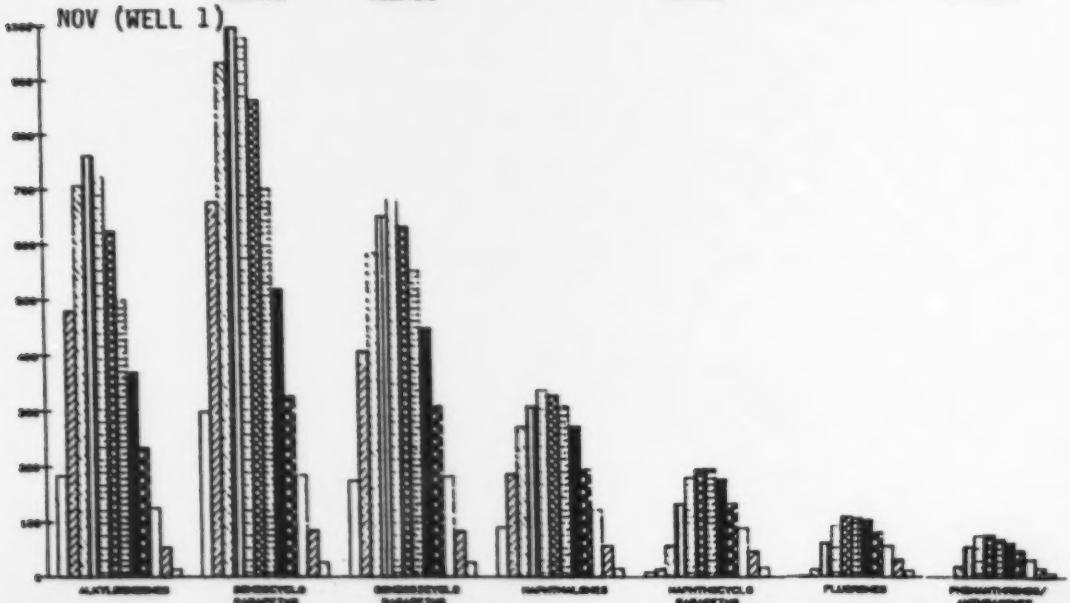


Figure 10 **Distribution of compound types in the saturates fraction of the distillation residue.**

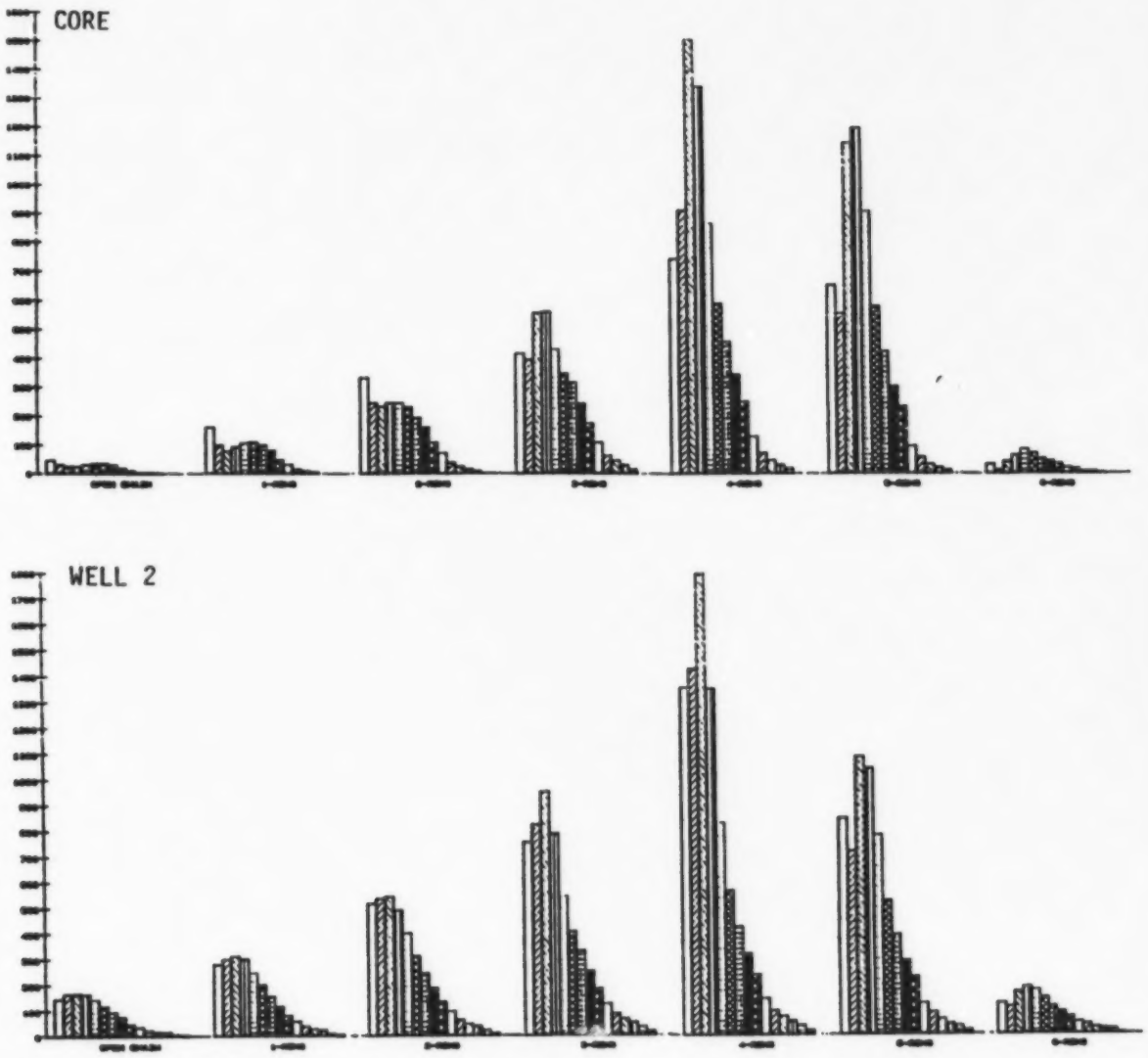


Figure 10 - con't

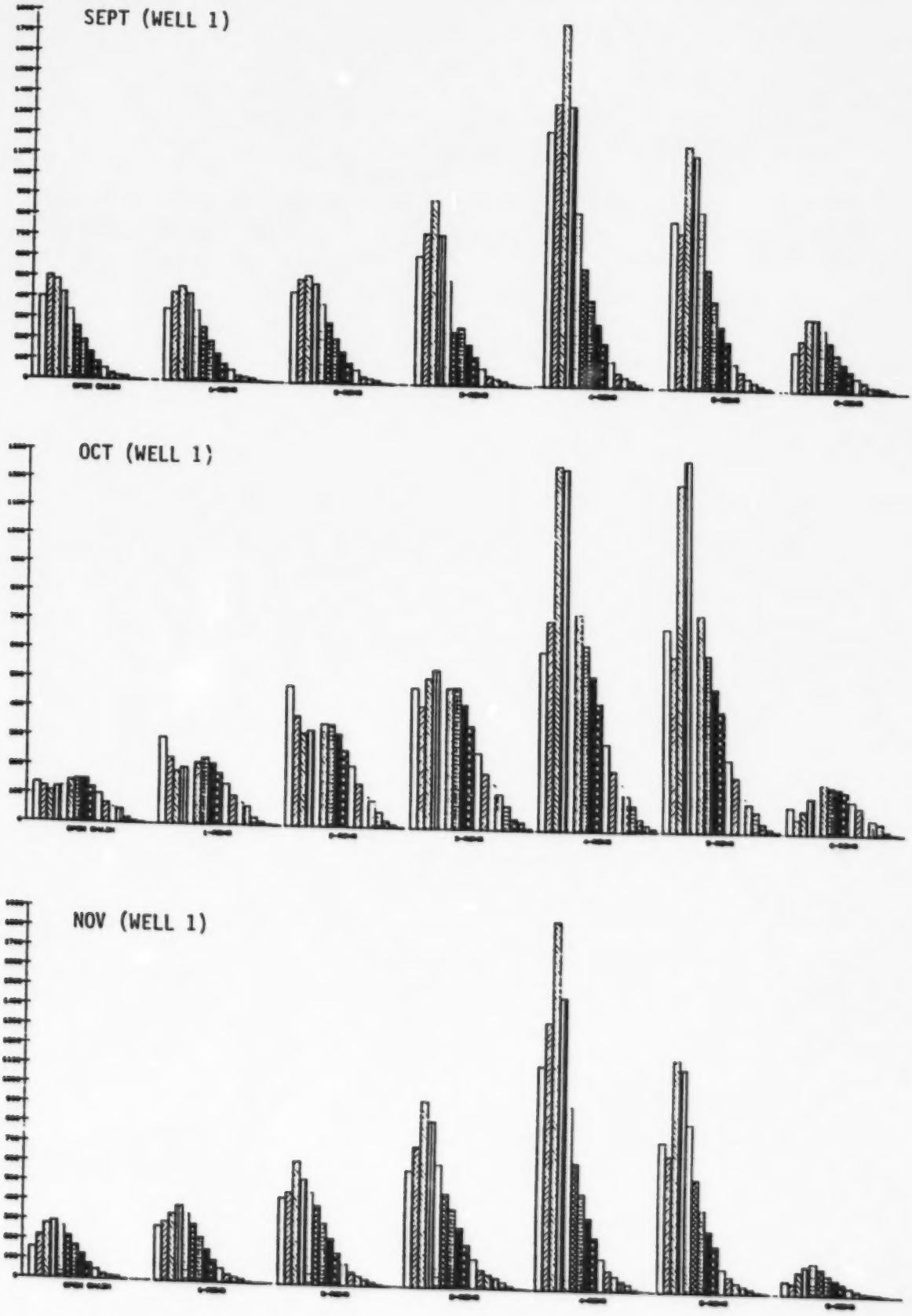


Figure 11 Distribution of compound types in the aromatics fraction of the distillation residue.

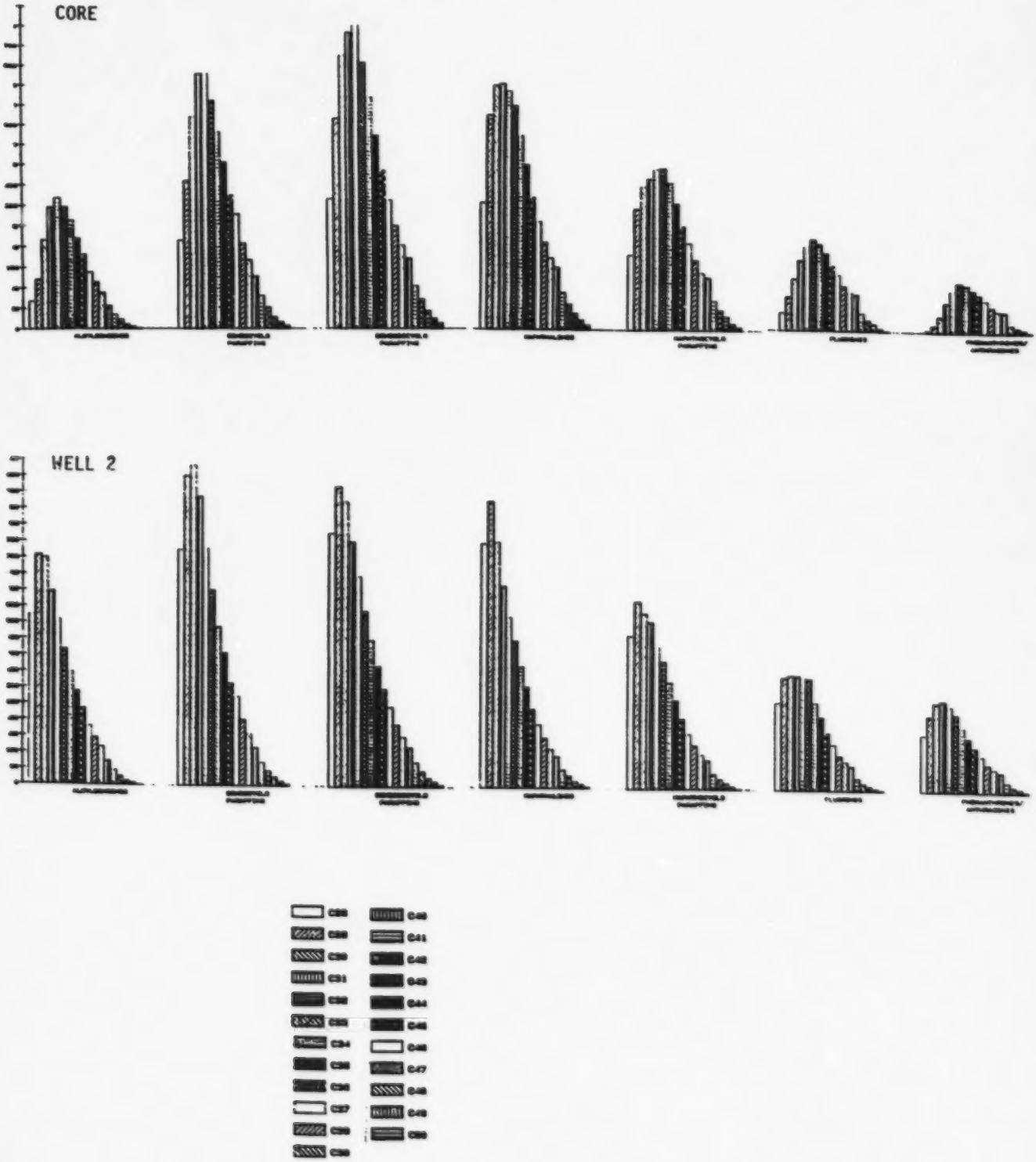


Figure 11 - con't